

## FIFTY YEARS OF VASKA'S COMPOUND (1)

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### Abstract

Textbooks in organometallic chemistry list *trans*-chlorocarbonylbis(triphenylphosphine) iridium (I) alongside the name “Vaska’s compound.” The year 2011 represents fifty years since the synthesis and characterization of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  by Prof. Lauri Vaska. From the perspective of the history of chemistry, this anniversary raises a number of questions. For example, who is Lauri Vaska? Vaska’s work on group 8 and 9 transition metal compounds led to the discovery of a number of low-valent complexes during the early days of the rapidly emerging field of organometallic chemistry. How did he discover the compound that bears his name? What is the significance of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  and when did the term “Vaska’s compound” first enter our vocabulary? We will also examine the question of whether or not Vaska really was the first to discover  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  and his connection to the discovery of Wilkinson’s catalyst.

### What Is Vaska’s Compound?

On April 20, 1961, the editors at the *Journal of the American Chemical Society* received a communication (2) from the Mellon Institute describing the synthesis and characterization of *trans*-chlorocarbonylbis(triphenylphosphine) iridium (I). To most organometallic chemists and in the indices of several textbooks (3), this compound is known as “Vaska’s compound” after Lauri

Vaska, who together with John W. DiLuzio, co-authored the aforementioned paper. At least one chemical supply house lists the compound (CAS 14871-41-1) in its catalogs under the name “Vaska’s compound” as well as by its chemical name (4). Among the thousands of transition metal organometallic compounds reported over the past half-century, what makes *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  special enough to be known by name? Who is Lauri Vaska and what path led to the synthesis of the compound that bears his name? As we celebrate the 50<sup>th</sup> anniversary of the discovery of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , this paper will explore the biography of Lauri Vaska, as well as the chemistry and history behind his compound.

### Who Is Lauri Vaska? (5)

Lauri Vaska was born on May 7, 1925, in the town of Rakvere in Estonia. At the time of his birth, Estonia, the northernmost of the Baltic countries, was enjoying independence for the first time in modern history. The turmoil that followed the end of the First World War on the Eastern Front and the subsequent events of the Bolshevik Revolution in Russia opened the door to independence for the Baltic countries, Estonia, Latvia and Lithuania. His father, a decorated veteran of the war for independence, earned his living as a surveyor. The family lived in the capital of Tallinn and maintained a farm in Rakvere. Vaska received his primary and secondary education both at the Riiklik Inglise Kolledž (State English College in Tallinn) and at the Rakvere Gümnaasium.

On the eve of the Second World War, Nazi Germany and the Soviet Union signed the Ribbentrop-Molotov Pact, ostensibly a non-aggression pact between the two nations (6). Included in the agreement were secret protocols that divided Eastern Europe into spheres of influence; the USSR was given the three Baltic States and half of Poland. Within a year, Soviet forces had fully occupied the Baltic countries and replaced the existing governments with Soviet-friendly regimes.

### Memories of 1940-1944

The German invasion of the Soviet Union in June 1941 exchanged Soviet masters for German rule. The Baltic States were occupied by the Wehrmacht by August 1941. Estonians would live under German rule for a little over three years. The five years of global conflict (1939-1944) saw Vaska grow from a 14-year old schoolboy to a 19-year old man. As the German lines crumbled in the summer of 1944 and once again brought the Red Army to the borders of pre-war Estonia, the teenager was conscripted into an Estonian unit serving with the Wehrmacht in the final defense of Estonia. During the turbulent summer of 1944, he served as a medical orderly until the front collapsed in September 1944 (5).

In the turmoil and confusion of the German Army's retreat from Estonia, Vaska and his family joined some 100,000 of his countrymen in escaping from Estonia in September 1944. Driven by memories of the recent Soviet occupation, many followed the Germans during their evacuation of the Baltic lands to refugee camps in Germany. May 8, 1945, finally brought an end to combat in the European theater and a division of Germany into four occupation zones, one each for the four victorious Allied Powers: the United States, the United Kingdom, France and the USSR.

### The Baltic University and the University of Göttingen

Life in a refugee camp in Germany in 1945 was a mixed blessing. Four years of war were over. On the one hand, the occupying authorities and the United Nations Relief and Rehabilitation Administration (UNRRA) ensured that the refugees were fed and housed (7). Conditions in the displaced persons (DP) camps were significantly better than for German citizens. On the other hand, Estonia remained occupied by the USSR. The forced deportation of the Baltic refugees from Germany back to their home countries, which the USSR

demanded based on their claim that the Balts were Soviet citizens, was prevented because the United States did not recognize the 1940 occupation of the Baltic States (8). As time passed in the DP camps, Baltic intellectuals and academics sought to start a "Baltic University" that would allow the refugees to continue their education (9). Conditions at German universities at the time did not allow for sufficient seats for refugees so permission was obtained from the British Army of the Rhine and the Hamburg DP University Centre (a. k. a. Baltic University) opened its doors in March 1946. Among the four Estonians who enrolled as chemistry undergraduates in May 1946 was Lauri Vaska (10). Although the Baltic University would last another three years and see up to 1200 students enroll, Vaska's stay was limited to one semester. By the fall semester, he had transferred to the Georg-August University in Göttingen. He recalls his first meeting with Prof. Hans von Wartenberg (11), head of the Göttingen inorganic chemistry institute, whose first question was "*Sind Sie ein DP?*" (12) During his undergraduate career, Vaska studied coordination chemistry and experimental inorganic chemistry with Prof. Josef Goubeau (13) and Raman spectroscopy with Prof. Franz Feher (14). The years 1946-1949 allowed the young chemist to attend lectures by Werner Heisenberg, witness the last public presentation by Max Planck and have a beer at the same bar as Otto Hahn and his group (15).

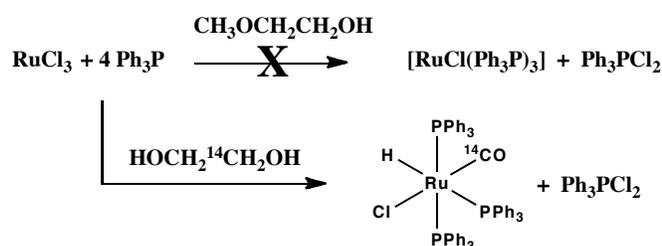
### Emigration and the University of Texas

A permanent solution to the problem of the Baltic DPs continued to elude the Allied authorities. Economic conditions in Germany were not conducive to settlement of the DPs in Germany and the escalation of the Cold War meant that the refugees refused to return to their occupied homeland. Slowly, other countries began to open their doors to these refugees. In 1949, the US Congress passed the Displaced Persons Act that allowed emigration to the United States (7c). By 1952 Vaska had emigrated to the United States and began graduate study at the University of Texas at Austin working with Prof. George W. Watt (16). His Ph.D. dissertation, "*Ammoniolysis of Potassium and Ammonium Hexabromoosmates*" focused on the use of ammonia as a solvent for transition metal chemistry. Watt's group worked with ammonia under familiar low temperature, ambient pressure conditions as well as under high pressures where reaction temperatures up to 90°C could be achieved (17). It was Watt who guided Vaska to the chemistry of the platinum group metals when he announced to his new graduate student that he would be working with osmium, handing him a 10-g vial of OsO<sub>4</sub>

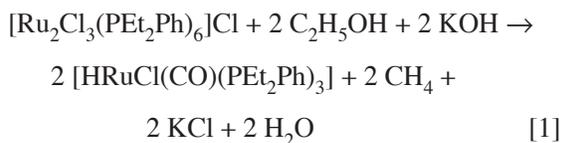
and telling him to make it last through his entire Ph.D. research (15).

### Lauri Vaska's Early Career

After a brief period of post-doctoral study at Northwestern University with Prof. Pierce W. Selwood (18), Vaska began his career as an assistant professor in 1957 at the Mellon Institute for Industrial Research in Pittsburgh, a predecessor of Carnegie-Mellon University (19). It was natural that he would continue his study of coordination chemistry of the group 8 and 9 metals, submitting his first paper to the *Journal of the American Chemical Society* in March 1960 (20). The title of the paper, "Univalent Ruthenium," reported the product of a reaction between ruthenium (III) chloride and triphenylphosphine in methoxyethyl alcohol as  $\text{ClRu}(\text{PPh}_3)_3$  (Figure 1). Somewhat fortunately, this paper has only been cited once, by Vaska himself, when he corrected the formulation of this compound to  $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$  (21). From the beginning of his career, Vaska's research would overlap with work from many better known inorganic chemists of the day. The recognition that the reported "univalent ruthenium" was indeed a hydrido ruthenium (II) carbonyl complex came after learning of Joseph Chatt's synthesis of hydridometal carbonyl halide complexes from metal halides and tertiary phosphines in ethanol (equation 1) in March 1960 (22).



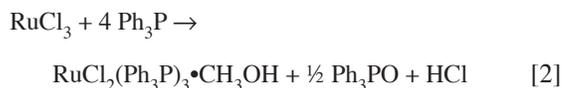
**Figure 1.** Reaction between ruthenium (III) chloride and triphenylphosphine in methoxyethyl alcohol as originally interpreted by Vaska (top) and then as corrected by Vaska.



The characterization of " $\text{ClRu}(\text{PPh}_3)_3$ " relied on elemental analysis, the determination of molar mass and

magnetic measurements. One can only speculate as to why Vaska did not report the IR spectrum until after the initial communication was published, as it surely would have led to the identification of the CO ligand. In his defense, one notes that the elemental analyses for C, H, P, Cl and Ru for " $\text{ClRu}(\text{PPh}_3)_3$ " and  $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$  are quite similar (23). The observed diamagnetism of the  $d^7$  "univalent ruthenium" was explained by an exchange interaction between neighboring ruthenium (I) atoms, analogous to work reported the previous year by others. The dawn of the 1960s was an era where the application of NMR spectroscopy to transition metal complexes was in its infancy, so the failure to detect the Ru-H bond by  $^1\text{H}$  NMR is excusable. In any event, both the CO and hydride ligands were identified by IR spectroscopy in Vaska's 1961 paper describing the correct composition of  $\text{HMCl}(\text{CO})(\text{PPh}_3)_3$  ( $\text{M} = \text{Ru}, \text{Os}$ ). In a further significant experiment using  $^{14}\text{C}$  labeled ethylene glycol, Vaska was able to trace the source of the carbonyl ligand to the  $\text{CH}_2\text{OH}$  group in the alcohol solvent (Figure 1).

The coordinatively saturated  $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$  has seen limited use as a hydrogenation catalyst. It is likely that Vaska was the first to discover the well known ruthenium (II) compound,  $\text{RuCl}_2(\text{PPh}_3)_3$ . In both his own writings (24) and in James Ibers' 1965 publication (25) of the crystal structure of  $\text{RuCl}_2(\text{PPh}_3)_3$  credit for the first synthesis of this compound is assigned to Vaska. Errors in the footnotes to the Ibers paper make it difficult to track the first report of  $\text{RuCl}_2(\text{PPh}_3)_3$ , however, it does appear that Vaska's claim is valid. A 1961 paper in the British journal *Chemistry and Industry* (26) reports the isolation of  $\text{RuCl}_2(\text{PPh}_3)_3$  as a green methanol solvate from a reaction between  $\text{RuCl}_3$  and triphenylphosphine in methanol at ambient temperature (equation 2). It is only under these relatively mild conditions that formation of ruthenium carbonyl complexes is avoided. The ruthenium (II) compound isolated in this manner has proven to be an active catalyst in organic chemistry and most importantly, is a precursor to the versatile hydrogenation catalyst  $\text{HRuCl}(\text{PPh}_3)_3$  (27). In light of his subsequent work on the reactivity of late-transition metal phosphine complexes with hydrogen, it is surprising that the conversion of  $\text{RuCl}_2(\text{PPh}_3)_3$  to the efficient homogeneous hydrogenation catalyst  $\text{HRuCl}(\text{PPh}_3)_3$  escaped his grasp.



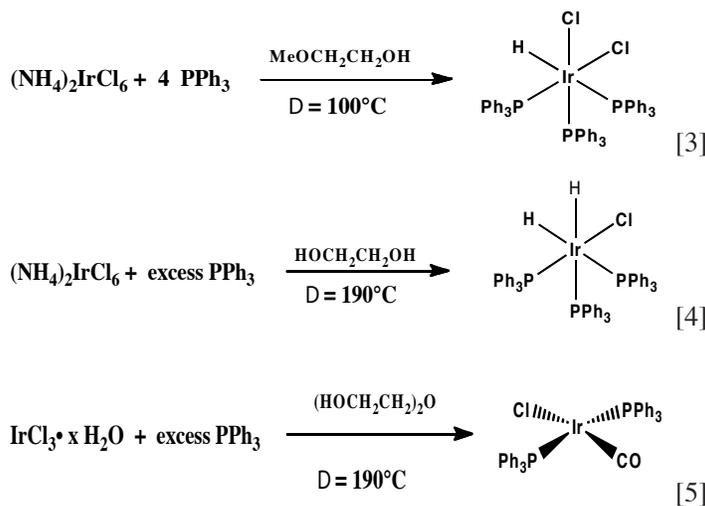
## The Discovery of Vaska's Compound

The observed reduction of late transition metal halides in the presence of phosphine in an alcohol solvent turned out to be important to Vaska's future work. In the same year that the synthesis of  $\text{RuCl}_2(\text{PPh}_3)_3 \cdot \text{MeOH}$  was reported, he published a short, single-author communication describing the synthesis of five iridium phosphine, arsine and stibine hydride complexes:  $\text{IrHCl}_2(\text{EPh}_3)_3$  ( $\text{E}=\text{P}, \text{As}, \text{Sb}$ ) and  $\text{IrH}_2\text{X}(\text{PPh}_3)_3$  ( $\text{X}=\text{Cl}, \text{Br}$ , equations 3 and 4) (28). The latter compounds were all prepared by heating  $[\text{NH}_4]_2[\text{IrCl}_6]$  and the corresponding group 15 ligand in alcohol solvent at temperatures ranging from ambient to  $190^\circ\text{C}$ . The Ir–H bond was identified by IR and no evidence is presented for the formation of iridium carbonyl complexes under these conditions. In light of his concurrent observations with ruthenium halide complexes, one concludes that indeed, Vaska did not miss a coordinated CO for a second time.

Within a few months, however, Vaska and John DiLuzio reported that when reaction conditions were altered, an entirely different product was isolated (2). Instead of six-coordinate octahedral iridium (III) complexes  $\text{IrHCl}_2(\text{PPh}_3)_3$  and  $\text{IrH}_2\text{Cl}(\text{PPh}_3)_3$ , a square planar iridium (I) product,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  precipitates from solution (equation 5). A possible intermediate,  $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$ , was isolated but could not be purified. The presence of the CO was clearly identified by IR spectroscopy and  $^{14}\text{C}$  labeling studies. Single crystal x-ray structures were obtained in 1988 and 1991 (29) so the formulation of the compound known as "Vaska's compound" is not in doubt. It remains unclear from the scientific literature (30) precisely what modifications were made to the procedure for preparing  $\text{IrHCl}_2(\text{PPh}_3)_3$  and  $\text{IrH}_2\text{Cl}(\text{PPh}_3)_3$  that instead yielded  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . The hydrido-iridium compounds and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  were obtained in excellent yield (87%  $\text{IrH}_2\text{Cl}(\text{PPh}_3)_3$  vs 86%  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ) from both hydrated  $\text{IrCl}_3$  and  $[\text{NH}_4]_2[\text{IrCl}_6]$  in ethylene glycol at the same temperature ( $190^\circ\text{C}$ ). The reported yields and reaction times for the preparation of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  are remarkably similar for a range of solvents:

86% yield after 2 h in 2-methoxyethanol at  $190^\circ\text{C}$ , 75% after 7 h in ethylene glycol at  $190^\circ\text{C}$ , 76% after 2 h in diethylene glycol at  $240^\circ\text{C}$  and 83% after 4 h in triethyleneglycol at  $270^\circ\text{C}$  (1). In his reminiscences (24) about those days, Vaska alludes to the role of "forgetfulness" in the initial synthesis of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . Did he really

leave a flask containing iridium chloride and triphenylphosphine in ethylene glycol accidentally at  $190^\circ\text{C}$  overnight? In his writings, he reveals that the synthesis of the aforementioned  $\text{RuCl}_2(\text{PPh}_3)_3$  was the result of leaving a 2-methoxyethanol solution of  $\text{RuCl}_3$  and  $\text{PPh}_3$  at  $20^\circ\text{C}$  for "a few weeks" (24) so perhaps it is true that luck played a critical role in the discovery of both  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . (31)



## How Did "Vaska's Compound" Get its Name?

Many important compounds have been discovered in the last 50 years. How did  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  earn its place among compounds known by their discoverer's name? It seems that the term "Vaska's compound" first appeared in our lexicon in 1966 (32). Three papers submitted in 1966 (published in 1967) use some version of the name "Vaska's compound. James Collman refers to "Vaska's iridium (I) complex" in a paper submitted on March 2, 1966 (32a), while Umberto Bellucco spells out "Vaska's compound" in an article in *Inorganic Chemistry* submitted in July of the same year (32c):

Furthermore, treating Vaska's compound with hydrogen halides, octahedral complexes of *cis*-hydrogen halide have been obtained, as confirmed by infrared spectra.

Clearly Vaska's name was already associated with  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  in the community as James Ibers also refers to it in his 1967 paper where he compares the chemistry of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  to his own observations on  $[\text{PtCl}(\text{CO})(\text{PPh}_3)_2]^+$  (32d):

The compound is now known to contain the new cation *trans*- $\text{PtCl}(\text{CO})(\text{PC}_2\text{H}_5)_2^+$ , which is isoelectronic

with Vaska's compound  $\text{IrCl}(\text{CO})(\text{PR}_3)_2$ , where R may be alkyl or aryl.

The well-known German chemist Walter Strohmeier also referred to  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  as "Vaska's compound" in 1968 (33). Later in the same year, James Collman joined the chorus as *Inorganic Syntheses* published the preparation of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  writing that (34):

The compound was first prepared by Angoletta, but was correctly formulated by Vaska, who first described its addition reactions. It is often referred to as 'Vaska's compound.'

### Was Vaska First?

The reference to Angoletta in *Inorganic Syntheses* raises the question of whether or not Vaska was the first to discover  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . Vaska admits (24) to being unaware of the work by an Italian chemist, Maria Angoletta, who reported on carbonyl derivatives of iridium in 1959 (35), two years before Vaska's report in the *Journal of the American Chemical Society*. Several reasons may account for credit for discovering  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  being assigned to Vaska and not to Angoletta. First, the *Journal of the American Chemical Society* enjoys a wider readership than the *Gazzetta Chimica Italiana*, so perhaps Vaska is correct when he writes that he was ignorant of work published in the latter periodical. Second, Angoletta refers to compounds containing two carbonyl ligands per iridium,  $\text{Ir}(\text{CO})_2(\text{PR}_3)_2\text{X}$  and  $\text{Ir}(\text{CO})_2(\text{AsR}_3)_2\text{X}$ , in her paper. As Collman mentions, it was Vaska who correctly formulated the composition of  $\text{IrCl}(\text{CO})(\text{PR}_3)_2$  as containing one CO per Ir. Finally, we can turn to the words of Walter Strohmeier in his 1968 review of homogeneous catalysis (33):

The elucidation of the mechanism in homogeneous catalysis requires that all reactants, intermediates, and end products can be characterized and isolated. In addition, the structure, composition, and molecular weight of the catalyst in solution must be known. Another requirement is the knowledge of the composition and structure of the intermediate formed between the catalyst and one of the reaction products. Extensive research on Vaska's compound,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , has yielded most of the information mentioned above.

### Why Is Vaska's Compound Important?

The recognition of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  as "Vaska's compound" and its inclusion in textbooks does not rest exclusively on his status as the discoverer of this square planar, coordinatively unsaturated iridium (I) compound.

Rather, it is the reactivity of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with small molecules that gives the compound its benchmark status in the field of transition metal organometallic chemistry. Even in his initial paper (2) on  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , the important chemistry of Ir(I) is revealed;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  reacts with HCl to yield  $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$  in a process known today as oxidative addition (3). The reactivity of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with HCl,  $\text{Cl}_2$  and  $\text{H}_2$  was investigated and discovered within a year of the original report on  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (36). The ability of a transition metal compound to activate H-H bonds at *ambient* temperature was fundamental to later discoveries of catalysts for the homogeneous hydrogenation of unsaturated organic substrates. The mechanisms of these reactions have been extensively studied and the results form the foundation of textbook chapters where the chemistry of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  is described (3). It is noteworthy that Vaska also reports (2) that reaction between  $\text{IrCl}_3$ ,  $\text{PPh}_3$  and 2-butenal yields small amounts of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . In retrospect, he may have even observed the activation of C-H bonds in aldehydes followed by decarbonylation and reductive elimination of alkane, processes that have been well documented for other coordinatively unsaturated metal complexes. Vaska's compound also reversibly coordinates small molecules such as CO,  $\text{SO}_2$  and  $\text{O}_2$  (37). It is the latter substrate that attracted a lot of attention as the reversible binding of oxygen to hemoglobin was one of the few other examples of this behavior among transition metal complexes.

### Lauri Vaska and Sir Geoffrey Wilkinson

The connection between Vaska's compound and the advances in homogeneous catalysis in the 1960s inevitably invites an exploration of the relationship between Lauri Vaska and Sir Geoffrey Wilkinson, with whom he shares proximate space in textbooks (3). Did Vaska have a hand in the discovery of  $\text{RhCl}(\text{PPh}_3)_3$ , known as "Wilkinson's catalyst?" If not, given his interest in  $\text{H}_2$  activation how did he miss the reactivity of both  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RhCl}(\text{PPh}_3)_3$  with hydrogen? The first report that  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  oxidatively adds  $\text{H}_2$  comes some six months after Wilkinson's report (26) of the homogeneous hydrogenation of olefins using  $\text{RhCl}(\text{PPh}_3)_3$ . Vaska recognized the possibility of using  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  ( $1.3 \times 10^{-3}$  M) as a hydrogenation catalyst in a paper received on August 9, 1965 (38), reporting 40% conversion of ethylene to ethane at 60°C after 18 hours under 290-620 mm Hg hydrogen pressure and 270-440 mm Hg ethylene pressure. Under the same conditions the rhodium analog of Vaska's compound,  $\text{RhCl}(\text{CO})$

(PPh<sub>3</sub>)<sub>2</sub>, is less active with only 24% conversion after 22 hours of reaction (39). In his paper, Vaska (38) cites Wilkinson's work on the catalytic activity of ClRh(PPh<sub>3</sub>)<sub>3</sub> in homogeneous hydrogenation published earlier in the same year. Curiously, a second footnote to the chemistry of ClRh(PPh<sub>3</sub>)<sub>3</sub> reads

This compound, discovered by us independently several years ago, is highly dissociated in solution, and its composition and structure in solution are unknown at present.

Is there any truth to Vaska's claim? Wilkinson noted in his 1965 paper (39b) that his group probably shared the discovery of ClRh(PPh<sub>3</sub>)<sub>3</sub> writing that the latter compound is

Obtained as red-purple crystals by the interaction of ethanolic solutions of RhCl<sub>3</sub>•3H<sub>2</sub>O with a ≈ 6-fold excess of triphenylphosphine acting as complexing and reducing agent and a suppressor of dissociation. This compound and the corresponding bromide and iodide have also been obtained by M. A. Bennett, University College, London (personal communication).

In fact, in Wilkinson's 1965 presentation on the catalytic activity of ClRh(PPh<sub>3</sub>)<sub>3</sub> at a Welch Foundation Conference on Chemical Research (40), there is no mention of Wilkinson having known of Vaska's claim. Nevertheless, years later Vaska wrote (24):

...replacing IrCl<sub>3</sub> with the corresponding isoelectronic rhodium chloride and leaving the rest of the ingredients the same, a sudden precipitation of a dark red substance occurs at ≈ 124°C. This precipitate persists but a few minutes (continued heating causes a color change to a yellow solution, from which the analogue to the iridium complex, *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> is isolated). After several experiments the dark red substance was isolated in chemically pure form. Analysis showed that we were dealing with a new complex RhCl(PPh<sub>3</sub>)<sub>3</sub>.

Vaska acknowledges that the same compound had been synthesized by an English and an Australian chemist before Wilkinson. Who were these unidentified chemists? In all likelihood, the "Australian" is Martin Bennett and the mystery Englishman may be Dr. Robin Coffey working at ICI. Prof. Bennett recalls that he and Coffey had also isolated RhCl(PPh<sub>3</sub>)<sub>3</sub> but were waiting to file a patent when Wilkinson beat them to the table (41). Bennett later published his synthesis of "Wilkinson's catalyst" around the same time as Wilkinson's initial report (42). In any event, Vaska recognizes that it was Wilkinson who suc-

cessfully used ClRh(PPh<sub>3</sub>)<sub>3</sub> in homogeneous catalysis; in 1992 he wrote, "You can't win them all" (23).

## Conclusions

Whether by accident or design, in Lauri Vaska's hands the reaction between iridium (III) chloride and triphenylphosphine in hot alcohol yielded a novel iridium(I) complex, IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, known today as Vaska's compound. Its importance lies in being the first compound to undergo oxidative addition reactions with a range of small molecule substrates and yield isolable, characterizable products. The chemistry of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> that Vaska uncovered and published between 1961 and 1965 contributed to the explosion of research in homogeneous catalysis during this time. The fundamental reaction pathways observed for Vaska's compound contributed to the development of numerous homogeneous catalysts. His research interests intersected with those of better-known giants in the burgeoning field of organometallic chemistry, notably Geoffrey Wilkinson and Joseph Chatt.

Derivatives of Vaska's compound abound (43); there are some 62 references to "Vaska's compound" in the literature. Surprisingly, his 1961 paper on the synthesis of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> has been cited only about 60 times. In contrast, there are over 2000 references to RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, a compound for which Vaska does not often get credit for discovering.

Between those "golden 60s" (24) and retirement from Clarkson University in 1990, Vaska continued his research into homogeneous catalysis, publishing an additional 61 papers. In retirement, Vaska has authored four books on his life growing up in Estonia, his post-war experiences as a refugee and later as an émigré in the United States. In the 50<sup>th</sup> anniversary year of the first published report of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, it is safe to say that "Vaska's compound" is worthy of inclusion in textbooks of organometallic chemistry and in the pantheon of historically important organometallic compounds.

## References and Notes

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- a) C. M. Lukehart, *Fundamental Transition Metal Organometallic Chemistry* Brooks/Cole, Monterey, CA, 1985.  
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  - a) G. Woodbridge, *UNRRA: The History of the United Nations Relief and Rehabilitation Administration*, Columbia University Press, New York, 1950.  
b) M. J. Proudfoot, *European Refugees: 1939-52*, Faber and Faber, London, 1957.  
c) M. Wyman, *DP: Europe's Displaced Persons, 1945-1951*, Cornell University Press, Ithaca, NY, 1988.
  - The fate of most other refugees from Eastern Europe was repatriation, voluntarily or forcibly. See Ref. 6.
  - E. Järvesoo, Ed. *Balti Ülikool Saksamaal, 1945-1949*, Toronto, 1991.
  - The author's father served as an associate dean of the Baltic University for chemistry before continuing his own studies toward a doctorate in chemistry at the University of Hamburg.
  - Prof. Hans von Wartenberg (1880-1960) had served as head of the Göttingen inorganic chemistry institute from 1933 to 1937, when he was forced to retire by the Nazi administration. During the war he worked at the Göttingen physics institute. After the collapse of the Nazi regime, he was reinstated in his previous position at the inorganic chemistry institute. See <http://www.kchn.pg.gda.pl/?p=history&lng=en> (accessed Nov. 5, 2012).
  - The refugees were not particularly popular among the German civilian population as they were seen as, among other things, thieves and the recipients of special treatment from the Allied Military Government.
  - Josef Goubeau (1901-1990) earned his doctorate from the University of Munich in 1926 and taught at the University of Göttingen between 1940 and 1951 when he moved to a professorship at the Technical University of Stuttgart. His research was in the synthesis and Raman spectroscopy of boron, silicon and phosphorus compounds. See <http://www.uni-stuttgart.de/hkom/presseservice/pressemittelungen/2001/32.html> (accessed Nov. 5, 2012).
  - Prof. Franz Feher (1903-1991) earned his doctorate in 1927 from the Technical University of Stuttgart on the chemistry of manganese oxides. After a stint in Dresden, he moved to Göttingen in 1942 as senior assistant in the Chemical Institute. In September 1949 he took a position as Professor of Inorganic and Analytical Chemistry at the University of Cologne where he explored sulfur chemistry. See M. Baudler, "Franz Feher (1903-1991): A Personal and Professional Portrait," *Eur. J. Inorg. Chem.*, **1998**, 2089-2105.
  - L. Vaska, "Ebatäpne Aatom," *Akadeemia*, **1998**, 1453-1491.
  - George Willard Watt (1911-1980) joined the faculty at the University of Texas at Austin in 1937 and retired from there in 1978. In 1943-45, he worked on plutonium in the Manhattan Project See <http://www.utexas.edu/faculty/council/2000-2001/memorials/Watt/watt.html> (accessed November 5, 2012).
  - The first of four publications from his doctoral research appeared in 1954:  
a) G. W. Watt, D. Gordon, G. D. Barnett, and L. Vaska, "Interaction of alkali metals and liquid ammonia. Catalysis by metals and alloys," *J. Ind. Eng. Chem.*, **1954**, 46, 1022-1024.  
b) G. W. Watt, and L. Vaska, "The synthesis of bromopentammineosmium (III) halides," *J. Inorg. Nucl. Chem.*, **1958**, 5, 304-307.  
c) G. W. Watt and L. Vaska, "The interaction of ammonium and potassium hexabromoosmate(IV) and liquid ammonia at 25°. II. Ammonia soluble products," *J. Inorg. Nucl. Chem.*, **1958**, 6, 246-251.  
d) G. W. Watt and L. Vaska, "The interaction of ammonium and potassium hexabromoosmate(IV) and liquid ammonia at -34° and 90°," *J. Inorg. Nucl. Chem.* **1958**, 7, 66-72.
  - Pierce W. Selwood (1905-1986) completed his Ph.D. at the University of Illinois in 1931. Following post-doctoral work at Princeton, he joined the faculty at Northwestern University in 1935 where he established an international reputation in magneto and surface chemistry. It was during his years at Northwestern than Vaska published his only paper with Prof. Selwood: L. Vaska and P. W. Selwood, "The mechanism of chemisorption: hydrogen on nickel at elevated pressures," *J. Amer. Chem. Soc.*, **1958**, 80, 1331-1335. In 1962, Prof. Selwood moved to the University of California Santa Barbara where he continued his work in inorganic chemistry and chemical education. See <http://texts.cdlib.org/view?docId=hb6z09p0jh&doc.view=frames&chunk.id=div00044&toc.depth=1&toc.id=> (accessed Nov. 5, 2012).
  - The Mellon Institute was founded in 1913 to perform contract research for industry. In 1967, the Mellon Institute merged with the Carnegie Institute of Technology to become Carnegie-Mellon University. During Vaska's time in Pittsburgh, he worked for the Mellon Institute.
  - L. Vaska and E. M. Sloane, "Univalent Ruthenium," *J. Amer. Chem. Soc.*, **1960**, 82, 1263.

21. L. Vaska and J. W. DiLuzio, "Complex carbonyl hydrides of osmium and ruthenium," *J. Amer. Chem. Soc.*, **1961**, 83, 1262-1263.
22. J. Chatt and B. L. Shaw, "A Novel Route to Hydrido and Carbonyl Complexes of Transition Metals," *Chem. Ind. (London)*, **1960**, 931.
23. Calculated for  $C_{54}H_{45}RuClP_3$ : 70.24 %C, 4.91 %H, 10.06% P, 3.84% Cl, 10.95% Ru, calculated for  $C_{55}H_{46}RuClP_3O$ : 69.36 %C, 4.87 %H, 9.76% P, 3.72% Cl, 10.61% Ru, and 1.7% O. Found initially in 1960 paper (Ref. 20): 69.09 %C, 4.89 %H, 9.85% P, 3.80% Cl, 11.27% Ru, with 1.8% O found upon re-analysis in the 1961 paper (Ref. 21).
24. L. Vaska, "Kuidas Leiutasin *trans*-[Ir(Cl)(CO){ $(C_6H_5)_3P$ ]<sub>2</sub>]," *Akadeemia*, **1992**, 1475-1513.
25. S. J. LaPlaca and J. A. Ibers, "A Five-coordinated d<sup>6</sup>-Complex: Structure of Dichlorotris(triphenylphosphine) ruthenium (II)," *Inorg. Chem.*, **1965**, 4, 778-783.
26. L. Vaska, "Interaction of Osmium and Ruthenium Halides with Triphenylphosphine, -arsine and -stibine in Alcohols" *Chem. Ind. (London)*, **1961**, 1402-1403. Vaska reports the formation of  $Ph_3PCl_2$  as a product of the reaction but in all probability sufficient moisture is present to hydrolyze the P-Cl bonds to triphenylphosphine oxide and HCl.
27. Reaction of  $RuCl_2(PPh_3)_3$  with hydrogen in the presence of a base (e.g., triethylamine) yields  $HRuCl(PPh_3)_3$  whose activity in olefin hydrogenation was first published six years later by P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, "Selective catalytic homogeneous hydrogenation of terminal olefins using tris(triphenylphosphine) hydridochlororuthenium(II); hydrogen transfer in exchange and isomerization reactions of olefins," *Chem. Commun.*, **1967**, 305-306.
28. L. Vaska, "Hydrido Complexes of Iridium," *J. Amer. Chem. Soc.*, **1961**, 83, 756.
29. a) M. R. Churchill, J. C. Fettinger, L. A. Buttrey, M. D. Barkan, and J. S. Thompson, "An Accurate X-ray Diffraction Study of Vaska's Compound, *trans*-IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, Including Resolution of the Carbonyl/Chloride Disorder Problem," *J. Organometal. Chem.* **1988**, 340, 257-266. b) A. J. Blake, E. A. V. Ebsworth, H. M. Murdoch and L. J. Yellowlees, "Vaska's Compound - Dichloromethane Solvate (1/2)," *Acta Cryst.*, **1991**, C47, 657-659.
30. From Ref. 2: "We now find that on further treatment of these reaction mixtures the interaction with the solvent proceeds to give hydrido-carbonyl and carbonyl complexes, the subjects of the present communication."
31. In reference 24, Vaska writes that, "In science the die rarely lands on six, and at best, drawing a joker [in poker] happens but once in a lifetime, if at all. So it is, [in science, success] comes by accident or is dictated by fate (which can, of course, be synonymous)."
32. a) J. D. Collman and W. R. Roper, "Synthesis and Oxidative Addition Reactions of a Phosphine Carbonyl Complex of Osmium (0)," *J. Amer. Chem. Soc.*, **1966**, 88, 3505-3508. b) J. D. Collman and J. W. Wang, "Acetylene Complexes of Rhodium and Iridium," *J. Amer. Chem. Soc.*, **1967**, 89, 844-851. c) U. Bellucco, U. Croatto, P. Uguagliati and R. Pietropaolo, "Electrophilic Attack upon *trans*-Bis(triethylphosphine) diphenylplatinum," *Inorg. Chem.*, **1967**, 6, 718-721. d) H. C. Clark, P. W. R. Corfield, K. R. Dixon and J. A. Ibers, "An Unexpected Product in the Reaction of  $PtHCl(P(C_2H_5)_3)_2$  with  $C_2F_4$ . The Structure of the  $PtCl(CO)[P(C_2H_5)_2]_3^{2+}$  Cation and Evidence for the Existence of the  $SiF_6^-$  Ion," *J. Amer. Chem. Soc.*, **1967**, 89, 1360-1361. e) L. Malatesta, "Some Recent Aspects of the Chemistry of Iridium" *Helv. Chim. Acta* **1967** 147-165.
33. W. Strohmeier, "Problem and Model of Homogeneous Catalysis," *Structure and Bonding (Berlin)*, **1968** 5, 96-117.
34. K. Vrieze, J. P. Collman, C. T. Sears Jr. and M. Kubota, "*Trans*-Chlorocarbonylbis(Tri-Phenylphosphine)Iridium," *Inorganic Syntheses*, **1968**, 11, 101-104.
35. M. Angoletta, "Derivati carbonilici dell'iridio.-Nota III. Alogenuri di dicarbonilamminoiridio (I)," *Gazz. Chim. Ital.*, **1959**, 89, 2359-2370. Prof. Maria Angoletta had a long and productive career in the Department of Inorganic, Organometallic and Analytical Chemistry at the University of Milan that stretched for over 30 years. She published over 40 papers on the chemistry of precious metals.
36. L. Vaska and J. W. DiLuzio, "Activation of Hydrogen by a Transition Metal Complex at Normal Conditions Leading to a Stable Molecular Dihydride," *J. Amer. Chem. Soc.*, **1962**, 84, 679-680.
37. a) L. Vaska, "Oxygen-carrying properties of a simple system," *Science*, **1963**, 140, 809-810. b) L. Vaska, "Reversible combination of CO with a synthetic oxygen carrier complex," *Science*, **1966**, 152, 769-771. c) L. Vaska and S. S. Bath, "Reversible Addition of Sulfur Dioxide to Four-Coordinated Metal Complexes," *J. Amer. Chem. Soc.*, **1966**, 88, 1333-1335.
38. L. Vaska and R. E. Rhodes, "Homogeneous Catalytic Hydrogenation of Ethylene and Acetylene with Four-Coordinated Iridium and Rhodium Complexes. Reversible Catalysts-Substrate Adducts," *J. Amer. Chem. Soc.*, **1965**, 87, 4970-4971.
39. a) F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, "Homogeneous Catalytic Hydrogenation and Hydroformylation of Acetylenic Compounds" *Chem. Ind. (London)*, **1965**, 560. b) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, "Hydride intermediates in homogeneous hydrogenation reactions of olefins and acetylenes using rhodium catalysts," *Chem. Commun.*, **1965**, 131-132. This manuscript was received on March 2, 1965, or six months before Vaska submitted the paper in reference 38.
40. G. Wilkinson, "Transition-metal to carbon bonds in aqueous solution and in catalysis," *Proceedings of the Robert A. Welch Foundation Conference on Chemical Research*, **1965**, (9), 139-161.

41. M. Bennett, personal communication. Bennett is actually an Englishman who has lived and worked in Australia for many years.
42. M. A. Bennett and P. A. Longstaff, "Complexes of rhodium(I) with triphenylphosphine," *Chem. Ind. (London)*, **1965**, 20, 846.
43. Some of the more recent papers include
  - a) R. N. Pandley and K. V. Gautam, "Synthesis and Spectral Characterization of Organometallic Derivatives of Palladium (0), Platinum (0), Rhodium (0) and Iridium (0) with Mixed Ligands," *Asian J. Chem.*, **2011**, 23, 4566-4568.
  - b) C. Douvris and C. Reed, "Increasing the Reactivity of Vaska's Compound. Oxidative Addition of Chlorobenzene at Ambient Temperature," *Organometallics*, **2008**, 27, 807-810.

### About the Author

Rein U. Kirss graduated from SUNY Buffalo in 1981 with a BA degree in History and a BS degree in Chemistry. A year later he completed a MS degree in Chemistry with Prof. O. T. Beachley Jr. before heading to the Midwest. He completed his Ph.D. in Inorganic Chemistry at the University of Wisconsin-Madison under the direction of Prof. Paul M. Treichel in 1986. After two years of post-doctoral study with Prof. Richard Eisenberg (University of Rochester) and a year as a research scientist at ATMI (Danbury, CT) he joined the faculty at Northeastern University in August 1989, where he has remained as an associate professor. He is co-author on three editions of *Chemistry: The Science in Context* (W. W. Norton, **2004**, **2009**, **2012**) and maintains research interests in the organometallic chemistry of iron and ruthenium.

## Chemical Heritage Foundation Names Carsten Reinhardt President and CEO

Carsten Reinhardt, professor of history of science at Bielefeld University will become president and CEO of the Chemical Heritage Foundation (CHF) effective August 1, 2013. He will be the third president of CHF, succeeding Thomas R. Tritton, who is retiring.

Reinhardt was selected following a worldwide search for a leader with a great depth of experience in the history of science and technology. He has extensively researched and published on the impact of chemistry on society through topics including the history of industrial research, the emergence of instrumentation, and chemistry's links to physics, biology, medicine, and technology.

Carsten Reinhardt joined the faculty of Bielefeld University in 2007. In 2006-2007 he held a fellowship at the Max Planck Institute for the History of Science. Prior to that, he spent a decade as a professor at the University of Regensburg.

The author of three books, most recently *Shifting and Rearranging: Physical Methods and the Transformation of Modern Chemistry* (Science History Publications/USA, 2006), Reinhardt has contributed to five edited volumes and published nearly forty scholarly articles. In addition he has received many awards and fellowships, including being named a fellow at the Max Planck Institute for the History of Science and professeur invité in the Department of Philosophy, École Normale Supérieure. Reinhardt was an Edelstein Fellow at CHF in 1998-1999. He was also an Edelstein Fellow at The Hebrew University of Jerusalem in 1994.

The Chemical Heritage Foundation is a collections-based nonprofit organization in Philadelphia, Pennsylvania, USA, that preserves the history and heritage of chemistry, chemical engineering, and related sciences and technologies. The collections are used to create a body of original scholarship that illuminates chemistry's role in shaping society. In bridging science with the humanities, arts, and social sciences, CHF is committed to building a vibrant, international community of scholars; creating a rich source of traditional and emerging media; expanding the reach of our museum; and engaging the broader society through inventive public events. For more information about CHF please visit our website at [www.chemheritage.org](http://www.chemheritage.org).