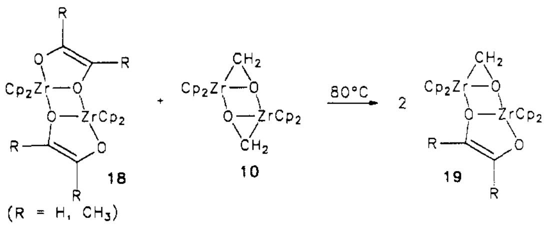

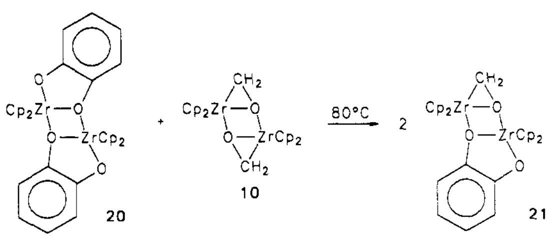

acceptor (at zirconium) compared to the five-membered metallacycle.

In the thermally induced reaction, the monomeric $Cp_2\overline{ZrOC}H_2$ intermediate most likely adds 1 equiv of the metal carbonyl. Carbon-carbon coupling then apparently occurs by means of a concerted electrocyclic ring closure reaction to give the five-membered metallacyclic zirconoxycarbene complex, which is then trapped by a second $Cp_2\overline{ZrOC}H_2$ species to give the observed stable product **12**. The addition of this molecular unit to $L_nM\text{-}C{\equiv}O$ thus represents another example of a nonnucleophilic route for the preparation of a heteroatom-stabilized carbene complex.

Acknowledgment. Generous financial support from the Volkswagen-Stiftung, the Fonds der Chemischen Industrie, NATO (Grant No. 0346/86), and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged. Miguel Mena thanks the Ministerio de Educacion y Ciencia, Madrid and the Alexander von Humboldt-Stiftung for a stipendium. Computer time for the X-ray structure refinement was provided by the West Virginia Network for Educational Telecomputing.

Supplementary Material Available: Tables listing thermal parameters, interatomic distances and bond angles, and least-squares planes (15 pages); a table listing the observed and calculated structure factors of **12d** (20 pages). Ordering information is given on any current masthead page.

Oxidation of the Ruthenium Hydride Complex $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)H$: Generation of a Dihydrogen Complex by Oxidatively Induced Intermolecular Proton Transfer

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Ruthenium hydride $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)H$ (**1**) undergoes a chemically irreversible oxidation at +0.39 V vs the ferrocene/ferrocenium couple. Oxidation of **1** with $(\eta^5\text{-}C_5H_5)_2Fe^+PF_6^-$ (**3**) in dichloromethane-d_2 yields the known dihydrogen complex $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^2\text{-}H_2)^+$ (**4**) as a primary decomposition product. Ferrocenium oxidation of **1** in acetonitrile-d_3 yielded $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(NCCD_3)^+$ (**2**-d_3), $HRu(CO)(PPh_3)(NCCD_3)_3^+$ (**5**-d_9), and cyclopentadiene. Cyclopentadiene and **5**-d_9 were generated via the prior formation of dihydrogen complex **4**. Solutions of independently prepared **4** in acetonitrile-d_3 were observed to decompose to yield some **2**-d_3, but mostly **5**-d_9 and cyclopentadiene. The results are discussed in terms of an initial proton transfer from cation radical $1^{\bullet+}$ to the Ru center of **1**, yielding **4**. It is proposed that a reversible, base-catalyzed deprotonation/protonation sequence generates an undetected cationic trans dihydride intermediate from which cyclopentadiene is eliminated.

Introduction

Transition-metal hydrides continually receive the attention of organometallic chemists because of their involvement in catalytic and stoichiometric processes.[2] The acidities of metal hydrides, in both the kinetic and the thermodynamic senses, in many cases have been systematically explored.[3] We recently reported the first estimates of metal hydride cation radical thermodynamic acidities in acetonitrile solution, noting that a number of group 6 hydride cation radicals were more acidic than their parent neutral hydrides by a relatively constant 20.6 ± 1.5 pK_a units.[4] All of the metal hydride cation radicals in that study were short-lived, their major mode of decomposition

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(1) (a) University of Oslo. (b) Utah State University.

(2) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987. (b) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147. (c) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988. (d) Carneiro, T. M. G.; Matt, D.; Braunstein, P. *Coord. Chem. Rev.* **1989**, *96*, 49.

(3) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179. (c) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (d) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945. (e) Kristjánsdóttir, S. S; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983. (f) Weberg, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1105.

(4) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618.

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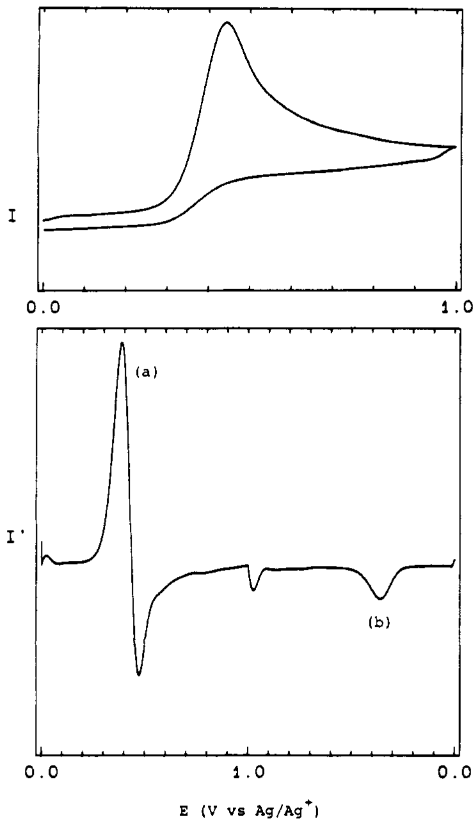

Figure 1. Cyclic voltammogram (top) and derivative cyclic voltammogram (bottom) for the oxidation of (η^5-C_5H_5)Ru(CO)(PPh_3)H (1; 1.0 mM) in acetonitrile/$Bu_4N^+PF_6^-$ (0.1 M) at a Pt microelectrode (d = 0.4 mm) at 20 °C and a voltage sweep rate v of 1.0 V/s.

being deprotonation. The proton acceptor was thought to be the reaction medium in most cases; for the cation radical of the least acidic hydride, (η^5-C_5H_5)W$(CO)_2$(PMe_3)H, proton transfer to the neutral parent hydride was observed.

Hoping to generate more stable metal hydride cation radicals, we initiated a study of the oxidative behavior of phosphine-substituted cyclopentadienylruthenium hydrides. Available acetonitrile pK_a data show that (η^5-C_5H_5)Ru$(CO)_2$H (pK_a = 20.2) is considerably less acidic than the group 6 counterparts (η^5-C_5H_5)M$(CO)_3$H (pK_a: Cr, 13.3; Mo, 13.9; W, 16.1).[3c] In view of the relatively constant acidity difference between neutral hydrides and their cation radicals noted above, we anticipated that this trend might be observed for the cationic ruthenium hydrides as well, resulting in thermodynamically, if not kinetically, more stable metal hydride cation radicals. In this paper we report the results of an investigation of the oxidative behavior of the ruthenium hydride complex (η^5-C_5H_5)Ru(CO)(PPh_3)H (1), which led to the observation of a new and unexpected mode of decomposition of a cationic dihydrogen complex.

Results

Electrochemical Oxidation of (η^5-C_5H_5)Ru(CO)(PPh_3)H (1). The electrochemical behavior of 1 was investigated with use of derivative cyclic voltammetry (DCV).[5] The differentiation of a normal cyclic voltammogram with respect to time offers several advantages. The base line problem arising from the double-layer charging current is effectively eliminated, allowing for the convenient use of DCV for the measurement of electrode reaction kinetics.[5b,6] In addition, the differential response allows for the resolution of details that may not be discernible in normal cyclic voltammograms. In this respect, we consider DCV to be even more sensitive than the semiderivative, or deconvolution, voltammetry technique recently applied by Philp, Reger, and Bond for the investigation of iron alkenyl E–Z isomerization reactions.[7]

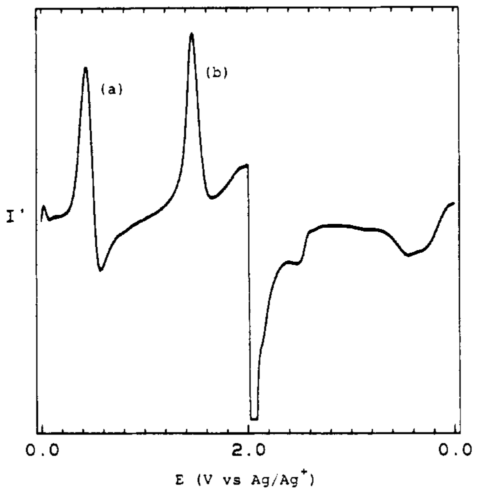

Figure 2. Derivative cyclic voltammogram of 1, showing the oxidation peak due to substrate oxidation (a) as well as a peak (b) attributed to the oxidation of the decomposition product (η^5-C_5H_5)Ru(CO)(PPh_3)(NCMe)$^+$ (2). Experimental conditions are as in Figure 1.

Figure 1 shows a normal cyclic voltammogram (top) and a DCV trace (bottom) for the oxidation of 1 (Pt-disk electrode, d = 0.4 mm, 293 K, acetonitrile/0.1 M Bu_4N^+-PF_6^-) at the voltage sweep rate v = 1.0 V/s. In the DCV trace, the cyclic voltammetry peak potential E_p for the oxidation of 1 corresponds to the point where the rapidly descending curve crosses the base line after the first derivative peak, labeled (a), and was found to be +0.39 V vs the ferrocene/ferrocenium couple (henceforth to be abbreviated FC). The differentiation process ensures readings of peak potentials more accurate than those available by normal cyclic voltammetry.[5b] The derivative peak width at half-height, $\Delta E_{p/2}$, which may give an indication about the reversibility of the electron-transfer process, was found to be 110 mV, indicative of quasi-reversible electron transfer.[4] The low intensity of the DCV peak on the reverse scan (b) indicates that cation $1^{\bullet+}$ undergoes complete reaction on the time scale of the measurements.[8] This observation pertained even at scan rates as high as 2000 V/s. Figure 2 shows the DCV trace of a scan that was taken to a more anodic potential. In addition to the oxidation peak for 1 (a), a peak due to oxidation of a de-

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(5) (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 73. (b) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

(6) For pertinent examples demonstrating the use of DCV in the study of electrode reaction kinetics of organometallic systems, see: (a) Aase, T.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4975. (b) Tilset, M.; Bodner, G. S.; Senn, D. R.; Gladysz, J. A.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 7551. (c) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757. (d) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *Organometallics* **1987**, *6*, 1628.

(7) Philp, R. H., Jr.; Reger, D. L.; Bond, A. M. *Organometallics* **1989**, *8*, 1714.

(8) When *derivative* cyclic voltammetry is used, a small peak is to be expected during the reverse scan even in the event that the electrode-generated species undergoes "complete reaction" on the time scale of the measurement. This behavior is caused by the "S"-shaped appearance of the reverse wave in the normal cyclic voltammogram and is observed even when the reverse peak has disappeared completely in the cyclic voltammogram.

composition product (b) can be seen. Seeding the solution with an equimolar amount of $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(NCCH_3)^+$ (2)[6a] as the BF_4^- salt caused this peak to double in intensity, suggesting that the product arising from decomposition of $1^{\bullet+}$ was indeed 2. The doubling of the peak intensity due to 2 indicates that the yield of 2 is essentially quantitative on the time scale of the measurements. We noted that severe adsorption problems and signal distortion arose when 2 was oxidized in the absence of 1, but not in its presence.

Constant-current coulometry with DCV monitoring of the disappearance of the substrate indicated the consumption of 1.70 ± 0.11 faraday/mol for the complete oxidation of 1. In the presence of 1 equiv of the hindered base 2,6-lutidine, the oxidation required the passage of 1.93 ± 0.15 faraday/mol. Constant-current exhaustive electrolysis (acetonitrile/0.05 M $Me_4N^+PF_6^-$) led to the formation of 2, identified by ^1H NMR and IR spectroscopy, as the only isolable product (92% isolated yield).

The measured E_p value for the oxidation of 2 was +1.39 V vs FC. Cation 2 also underwent a reduction process with $E_p = -2.03$ V vs FC. Steady-state reduction of 2 at −2.5 V vs FC, followed by a DCV scan initiated in the anodic direction, revealed a well-defined oxidation wave with $E_p = -1.05$ V vs FC. We assume that this wave is due to the oxidation of the anion $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)^-$, generated by the reductively induced loss of acetonitrile from 2. This is in accord with the observation that other cationic systems containing CO, phosphine, and acetonitrile ligands undergo preferential acetonitrile loss upon reduction.[4,9]

Homogeneous Chemical Oxidation of Ruthenium Hydride 1 in Dichloromethane-d_2. In our previous investigation of the oxidation of group 6 metal hydrides,[4] we experienced that the electrolytes commonly used by us for electrochemical studies were sufficiently basic that primary decomposition products might undergo unwanted deprotonation reactions. Thus, the dihydride $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H_2^+$, one product arising from the homogeneous oxidation of $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H$, was quite stable in *dry* acetonitrile but underwent spontaneous deprotonation in acetonitrile/0.1 M $Bu_4N^+PF_6^-$. Chemical oxidations in the absence of electrolytes then provide a means for observing products or intermediates that have insufficient lifetimes to be observed under preparative electrochemical conditions. The oxidation of 1 with chemical oxidants in carefully dried solvents was explored in order to facilitate the isolation and/or identification of decomposition products arising from possible intermolecular proton-transfer reactions.

The ^1H NMR spectrum of 1 in dichloromethane-d_2 displays a cyclopentadienyl singlet at δ 4.94 and a doublet arising from the hydride ligand at δ −11.77. Treatment of this solution of 1 (concentration ca. 18 mM) with 1 equiv of $(\eta^5\text{-}C_5H_5)_2Fe^+PF_6^-$ (3) at −100 °C[10] caused the gradual disappearance of the signals arising from 1. The major product, accounting for about half of the cyclopentadienyl-containing products, was the known[11] dihydrogen complex $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^2\text{-}H_2)^+$ (4). This product was readily identified by means of its characteristic broad $\eta^2\text{-}H_2$ resonance at δ −7.1 and the cyclopentadienyl singlet at δ 5.42. These assignments were confirmed by comparison with an authentic sample, prepared as described previously[11] from 1 and $HBF_4 \cdot Et_2O$. In addition, several cyclopentadienyl singlets were observed in the region δ 4.2–5.0. The cyclopentadienyl signals arising from 1 and 4 were sharp and well-defined at this temperature, as was the hydride doublet of 1. At −45 °C, considerable amounts of 1 were still present. At this temperature, the cyclopentadienyl and hydride signals of 1 and 4 had undergone significant line broadening, most likely due to fast-exchange processes between 1 and 4 in solution (vide infra). Upon further heating of the sample, the signals due to 1 slowly disappeared as the oxidation process went to completion. At +10 °C, 4 still accounted for half of the cyclopentadienyl-containing products. Four other cyclopentadienyl singlets at δ 4.92, 4.83, 4.67, and 4.45 (relative intensities ca. 1:1:2:2) accounted for the rest, but the products that gave rise to these signals remain unidentified.

Chemical Oxidation of 1 in Acetonitrile. The oxidation of hydride 1 (concentration ca. 18 mM) with 0.90–0.95 equiv of 3 in acetonitrile-d_3 initially appeared to lead to chemistry quite different from that described above. Thus, at room temperature the only detectable products were $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(NCCD_3)^+$ (2-d_3), $HRu(CO)(PPh_3)(NCCD_3)_3^+$ (5-d_9), and cyclopentadiene. The product 2-d_3 was identified by comparison of its ^1H NMR [δ 5.16 (s), $\eta^5\text{-}C_5H_5$] and IR (ν_{CO} 1988 cm^{-1}) spectra with those of an authentic sample.[6a] The other cationic product, 5-d_9, displayed a doublet at δ −13.77 ($J_{P-H} = 25.3$ Hz) in the ^1H NMR spectrum, and the IR spectrum showed an absorption at 1960 cm^{-1}. These data matched those for an independently prepared sample of 5 (vide infra). Cyclopentadiene was identified by its ^1H NMR spectrum [δ 2.97 (m, 2 H), 6.48 (m, 2 H), 6.55 (m, 2 H)], which was identical with that of an authentic sample, and by GLC–MS analysis. The yields of 2-d_3 and cyclopentadiene, based on consumed 1, were 56% and 33%, respectively, at 88% substrate conversion (^1H NMR, hexamethylbenzene internal standard).

The oxidation was repeated in acetonitrile-d_3 at −40 °C in an attempt at observing intermediates along the reaction path leading to loss of cyclopentadiene. Immediately after mixing of the reactants, the ^1H NMR spectrum showed the presence of cyclopentadiene, 2-d_3, 5-d_9, and a broad, dominating signal at δ 5.09 (peak width at half-height ca. 25 Hz). The hydride or cyclopentadienyl signals normally expected from 1 and 4 were not present. When the sample was heated, the signal at δ 5.09 vanished, with a concomitant increase in the intensities of the other product peaks. Eventually, as the reaction was complete, the presence of a small amount of unconsumed 1 was apparent from the spectrum.

In the presence of 1 equiv of 2,6-lutidine, the complete oxidation of 1 in acetonitrile-d_3 (18 mM) required 2 equiv of oxidant 3. In this case, the cation 2-d_3 was the only observable product derived from 1 (90%, ^1H NMR). On the preparative scale, 2 was isolated in 62% yield from a similar reaction carried out in acetonitrile (see Experimental Section for details).

Decomposition of $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^2\text{-}H_2)^+$ (4) in Acetonitrile-d_3. The ^1H NMR spectrum of a freshly prepared sample of 4 dissolved in acetonitrile-d_3 at −40 °C displayed the expected broad resonance due to the dihydrogen ligand at δ −7.1. However, the cyclo-

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[9] See for example: (a) Kochi, J. K. In *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*; Chanon, M., Julliard, M., Poite, J. C., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1989; p 149. (b) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087. (c) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1987**, *6*, 129. (d) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Organometallics* **1987**, *6*, 1886.

[10] $(\eta^5\text{-}C_5H_5)_2Fe^+PF_6^-$ is only sparingly soluble in dichloromethane even at ambient temperature, and therefore, the effective concentration of the oxidant in solution was considerably lower than that of 1.

[11] (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

pentadienyl resonance at δ 5.40 appeared broader than expected, especially when compared with the spectrum recorded in dichloromethane-d_2. In situ preparation of 4 from 1 and excess $HBF_4{\cdot}Et_2O$ in acetonitrile-d_3 at −40 °C led to the observation of a *sharp* cyclopentadienyl singlet for 4 at δ 5.44. When the sample containing 4 only was heated, the broad cyclopentadienyl resonance eventually disappeared. The major decomposition products were cyclopentadiene and $HRu(CO)(PPh_3)(NCCD_3)_3^+$ (**5**-d_9). Some **2**-d_3 also formed, but the yield of this product was only in the range 5–10%.

We suspected that the broadening of the cyclopentadienyl signal of 4 was due to the presence of minute amounts of 1, formed in the deprotonation of 4 by adventitious traces of water or other basic impurities. The presence of 1 could cause rapid proton-exchange processes between 1 and 4, leading to the observed line broadening. In order to investigate this possibility, a solution of a 1:1 mixture of 1 and 4 in acetonitrile-d_3 was studied by ^1H NMR spectroscopy. At −40 °C, signals due to cyclopentadiene, **5**-d_9, and a trace of **2**-d_3 were present, but no traces of 1 or 4 were to be seen. A broad resonance was observed at δ 5.35, most likely due to a rapid exchange process between 1 and 4. A control experiment showed that 1, although sparingly soluble, was soluble enough that its presence normally should have been readily detected at −40 °C. The poor solubility of 1 would explain why the observed cyclopentadienyl signal was not located at the arithmetical average of those for 1 and 4 separately. When the sample containing 1 and 4 was heated, the resonances arising from cyclopentadiene, **5**-d_9, and **2**-d_3 increased in intensity, and eventually the signals expected from 1 reappeared. Importantly, the decomposition of 4 took place much faster in the presence of added 1 than in its absence, as indicated by significant decomplexation of 4 even at −40 °C.

Synthesis and Characterization of $HRu(CO)(PPh_3)(NCCH_3)_3^+PF_6^-$ ((5)PF_6). Treatment of 1 with excess $HBF_4{\cdot}Et_2O$ in acetonitrile-d_3 (−40 °C) led to the smooth formation of 4, the cyclopentadienyl resonance of which (δ 5.44) was a sharp and well-defined singlet in the presence of excess HBF_4. This solution was stable at −40 °C. Most notably, no cyclopentadiene was observed even after 30 min at −15 °C. On the other hand, treatment of 1 with excess *aqueous* HBF_4 or HPF_6 under otherwise identical conditions initially gave 4, but within minutes the solution of 4 underwent further reaction to produce cyclopentadiene and **5**-d_9 in high yields, along with a trace of **2**-d_3. We took advantage of this observation for the independent synthesis of 5. Thus, treatment of 1 in acetonitrile with excess aqueous HPF_6 at 0 °C, followed by workup and recrystallization from acetonitrile/ether, gave (5)PF_6 (60%) as a white powder. The product appeared pure by IR (ν_{CO} 1960 cm^{-1}) and ^1H NMR [dichloromethane-d_2: δ −13.70 (d, J = 23.9 Hz, 1 H), 1.89 (s, 3 H), 2.02 (br s, 3 H), 2.36 (s, 3 H), 7.4–7.6 (m, 15 H)] spectroscopy. Assuming a pseudooctahedral coordination geometry at the metal center, the presence of three separate acetonitrile resonances indicates a facial relationship between these groups, and the magnitude of the phosphorus–hydride coupling constant is suggestive of a cis arrangement of the hydride and phosphine ligands. Further support for the structure assigned to 5 comes from the observation that, when treated with PPh_3, it smoothly provided the hexafluorophosphate salt of the known complex[12] $HRu(CO)(PPh_3)_2(NCCH_3)_2^+$ (**6**). The IR and ^1H NMR spectra of this product matched those of an authentic sample, prepared in analogy with the previously reported perchlorate salt.[12] The ^1H NMR spectrum of **6** (see Experimental Section) features a hydride triplet and two acetonitrile resonances, in accord with a mutual trans disposition of the two phosphine ligands and a cis disposition of the two coordinated acetonitrile units.

Treatment of 1 in acetonitrile with excess 50% aqueous H_2SO_4 also yielded cyclopentadiene. Repeating the reaction with 50% D_2SO_4 in D_2O led to the incorporation of only *one* deuterium into the cyclopentadiene molecule (GLC–MS analysis).

Finally, it should be mentioned briefly that the oxidation of the closely related hydride $(\eta^5\text{-}C_5H_5)Ru(CO)(PMe_3)H$ with 3 also leads to partial loss of cyclopentadiene. However, in this case this is not the major decomposition reaction. The details of this reaction will be reported in due time.

Discussion

Thermodynamic Acidity of a Ruthenium Hydride Cation Radical. The difference in thermodynamic acidities of a neutral metal hydride M–H and its cation radical $M\text{–}H^{\bullet+}$ may be estimated from eq 1, on the basis of a thermochemical cycle presented previously.[4] Here,

$$pK_a(M\text{–}H^{\bullet+}) = pK_a(M\text{–}H) + (F/2.301RT)[E^\circ_{ox}(M^-) - E^\circ_{ox}(M\text{–}H)] \quad (1)$$

$E^\circ_{ox}(M\text{–}H)$ and $E^\circ_{ox}(M^-)$ represent the reversible oxidation potentials for the metal hydride and its conjugate base (anion), respectively. Using the DCV potentials reported in this study for the oxidation of 1 (+0.39 V vs FC) and $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)^-$ (−1.05 V vs FC) provides an estimate for the pK_a difference between 1 and $1^{\bullet+}$ of 24.8 pK_a units. Due to the irreversible nature of both oxidation processes, this number should be viewed only as an approximate estimate. The pK_a difference appears to be quite similar to the corresponding pK_a difference of 20.6 ± 1.5 pK_a units for a number of group 6 cyclopentadienylmetal hydrides.[4] The anion oxidation potentials in these cases were corrected for kinetic shifts due to rapid radical dimerization. Application of a suitable kinetic shift correction[13] (assuming dimerization rate constants of 10^8–10^9 M^{-1} s^{-1} [14a]) to the present system causes the calculated difference in pK_a values between 1 and $1^{\bullet+}$ to be lowered to about 23 pK_a units.

No data have been published to date regarding the thermodynamic acidity of 1. It has been observed that the introduction of one PPh_3 ligand in $Co(CO)_4H$[3c] and $Mn(CO)_5H$[3e] leads to pK_a increases of 7.1 and 6.3 pK_a units. Making the rather crude assumption that the introduction of one PPh_3 ligand in $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ (pK_a = 20.2[3c]) has a similar effect leads to an estimated pK_a for 1 in the range 27–28. As a result, the pK_a of cation radical $1^{\bullet+}$ in acetonitrile is estimated to be around 4–5, comparable to that of $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H^{\bullet+}$.[4]

Deprotonation of the Cation Radical $1^{\bullet+}$. Product distributions from both the electrochemical and the chemical oxidation of 1 strongly suggest that the cation radical undergoes a net deprotonation reaction to give the final products. Deprotonation reactions have been frequently observed for metal hydride cation radicals.[4,15]

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[12] Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60.

[13] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980.

[14] (a) References to the dimerization rate constants for some 17-electron radicals may be found in ref 14b. (b) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125.

During electrolysis, the electrolyte medium appears to be basic enough to cause proton removal from $1^{\bullet+}$, since product **2** forms in high yields on the cyclic voltammetry time scale. The consumption of 2 faraday/mol in the presence of 2,6-lutidine (electrolysis as well as ferrocenium oxidation) is in accord with the overall transformation of eq 2, with 2,6-lutidine acting as a base.

$$(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)H \xrightarrow[CH_3CN]{-2e^-} (\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(NCMe)^+ + H^+ \tag{2}$$

Experimental evidence demonstrates that the medium was not basic enough to cause the proton removal during the ferrocenium oxidation of **1** in dry dichloromethane-d_2 or acetonitrile-d_3. The initial formation of **2**-d_3 and **4** (acetonitrile-d_3, −40 °C) suggests that neutral hydride **1** acted as a base toward $1^{\bullet+}$, as shown in Scheme I (eq 3). Oxidation of the resulting radical (**7**), presumably via the intermediacy of a 19-electron acetonitrile adduct,[16] would generate **2** (eq 4). Although the proton transfer from $1^{\bullet+}$ to **1** appears a likely sequence of events, we cannot exclude an alternative path[16] involving hydrogen atom transfer from **1** to $1^{\bullet+}$ that would also generate **4** and **7**. A hydrogen atom transfer between two cation radicals $1^{\bullet+}$, resulting in the initial production of **4** and the 16-electron cation $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)^+$, also should be considered.

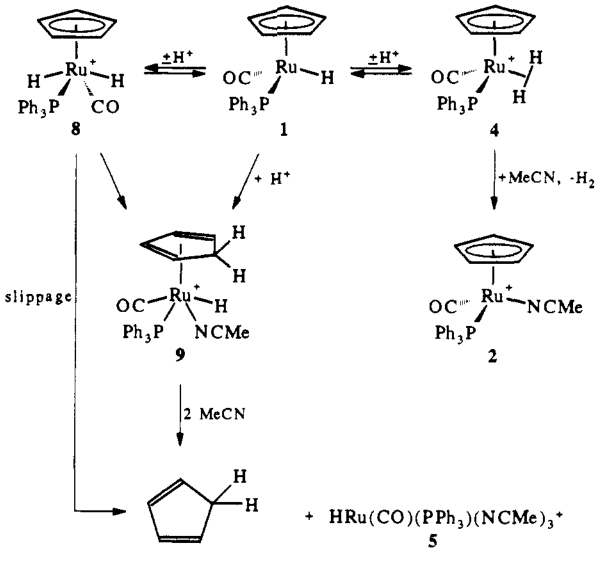
Cyclopentadiene Loss from Dihydrogen Complex 4. The literature provides numerous examples showing that dihydrogen ligands may be readily displaced by a variety of two-electron-donor ligands.[17] We therefore anticipated that acetonitrile would displace the dihydrogen ligand in **4** to form **2** after the initial proton-transfer reactions resulting from the oxidation of **1**. Surprisingly, loss of cyclopentadiene with concomitant formation of $HRu(CO)(PPh_3)(NCMe)_3^+$ (**5**) was by far the most important mode of decomposition of **4**. Such reactivity was observed not only when **4** was generated by oxidation of **1** but also when independently prepared **4** was dissolved in acetonitrile-d_3 at −40 °C and heated slowly to ambient temperature. The presence of excess $HBF_4\cdot Et_2O$ effectively prevented this reaction from taking place, whereas the addition of hydride **1** or *aqueous* HBF_4 or HPF_6 greatly accelerated the decomposition reaction. These observations are in agreement with a base-induced or base-catalyzed decomposition of **4** in acetonitrile. The base may be adventitious water or other basic impurities in solution, the water content of aqueous acids, or even the neutral hydride **1**. The active involvement of a base in this reaction positively excludes an intramolecular proton transfer from the dihydrogen ligand to the cyclopentadienyl ring as a mechanistic possibility. It also excludes intramolecular proton transfer to the ring from a *cis*-dihydride that could arise from oxidative addition of the dihydrogen ligand in **4**, and also an intramolecular rearrangement to the *trans*-dihydride **8**. The occurrence of facile equilibria between dihydrogen and dihydride complexes has been demonstrated in several instances.[11,17c,18]

Scheme I

$$\underset{\mathbf{1}}{(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)H} + \underset{\mathbf{1}^{\bullet+}}{(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)H^{\bullet+}} \longrightarrow \underset{\mathbf{4}}{(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^2\text{-}H_2)^+} + \underset{\mathbf{7}}{(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)^\bullet} \tag{3}$$

$$\underset{\mathbf{7}}{(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)^\bullet} \xrightarrow{+MeCN,\ -e^-} \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(NCMe)^+} \tag{4}$$

Scheme II



The experimental evidence suggests that an intermolecular proton-transfer process is operative. Such a process provides a route to the *trans*-dihydride **8**, which (although never observed) may be an intermediate in the decomposition reaction (Scheme II). The occurrence of an *inter*molecular dihydrogen–*trans*-dihydride rearrangement is in contrast with the *intra*molecular isomerizations recently encountered in a number of $(\eta^5\text{-}C_5H_5)RuL_2(\eta^2\text{-}H_2)^+$ (L = tertiary phosphine) complexes.[11b] However, these findings need not be at odds: Rapid self-exchange of **4** with its conjugate base **1** (acetonitrile-d_3, −40 °C) was indicated by the broadened ^1H NMR spectra obtained from mixtures of the two. For the bis(phosphine) analogues, Chinn and Heinekey observed separate peaks for the cationic dihydrogen complex and its parent hydride under similar conditions and could detect self-exchange only by using the relatively slow spin saturation transfer technique.[11b] In view of this, the rapid intermolecular proton transfer occurring in our system could conceivably mask a slower intramolecular dihydrogen–*trans*-dihydride isomerization reaction.

Two routes that differ in the timing of acetonitrile attack on intermediates appear likely for the conversion of **8** to the final product **5**. One alternative involves an endo

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electrophilic attack at the ring, accompanied by acetonitrile ligation, yielding the intermediate cyclopentadiene complex **9**. Alternatively, **8** could undergo a solvent-induced $\eta^5\text{-}C_5H_5 \rightarrow \eta^3\text{-}C_5H_5 \rightarrow \eta^1\text{-}C_5H_5$ ring-slippage[19] sequence terminated by reductive elimination of cyclopentadiene (overall sequence depicted as "ring slippage" in Scheme II). There is strong evidence that cationic dihydrogen complexes are considerably more acidic than their dihydride analogues.[11,20] For a series of dihydrogen and dihydride complexes containing the $(\eta^5\text{-}C_5H_5)Ru(PR_3)_2^+$ fragments ($2\ PR_3 = 2\ PPh_3$, dppm, dppe, dppp[21]), it has recently been shown[20] that the *cis*-dihydrogen complexes are more acidic than the related *trans*-dihydride species by about 1 order of magnitude. Thus, although **4** appears to be the kinetic product of the proton-transfer reaction (in agreement with recent observations in related systems[11b]), **8** would be anticipated to be thermodynamically more stable than **4**. If **8** is indeed an intermediate in the decomplexation reaction, then the failure to detect this intermediate even at low temperatures must imply that the rate of its decomplexation to yield **5** is considerably higher than its rate of formation by protonation of **1**. An alternative mechanism providing direct access to **9** without the intermediacy of **8** involves direct protonation at the ring (Scheme II). Ambiguities regarding the site of electrophilic attack in related systems exist in some cases.[22] However, conclusive evidence for direct electrophilic attack on the ring appears to be nonexistent, rendering such a process less likely. Regardless of the reaction mechanism, we note the similarity between the decomplexation found here and the observed slow loss of cyclopentadiene from $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ in acetonitrile.[3a]

The decomposition of **4** clearly is dependent on the presence of basic species in solution. In the presence of excess $HBF_4{\cdot}Et_2O$, the medium contains no species basic enough to effect the equilibration between **4** and *trans*-dihydride **8** or other intermediates. The presence of excess strong bases would also preclude this equilibration, because **4** would undergo spontaneous deprotonation to yield **1** only. Aqueous acids appear to be basic enough to facilitate the proton-transfer equilibration. Neutral hydride **1**, itself a postulated intermediate in the reaction, also may act as a base and as such is an interesting catalyst for the decomposition of the dihydrogen complex. ^1H NMR spectra show **1** and **4** to equilibrate rapidly even at −40 °C in acetonitrile-d_3 and dichloromethane-d_2. Chinn and Heinekey[11] reported facile proton exchange between $(\eta^5\text{-}C_5H_5)Ru(dmpe)H$[21] and $(\eta^5\text{-}C_5H_5)Ru(dmpe)(\eta^2\text{-}H_2)^+$ in acetonitrile-d_3. The attainment of proton-transfer equilibria between neutral hydrides and corresponding protonated species (dihydrogen or dihydride complexes) recently formed the basis for the quantitative evaluation of dihydride vs dihydrogen ligand acidities.[20]

Complex reaction mechanisms are often found for the deprotonation of organic cation radicals.[23] With this in mind, it is clear that mechanistic studies are still needed in order to determine the finer details of the metal hydride cation radical deprotonation reactions. We hope to resolve some of the still open questions in this regard through investigation of the deprotonation reactions of less reactive metal hydride cation radicals currently being undertaken in our laboratories.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile and acetonitrile-d_3 were distilled from P_2O_5 and CaH_2, respectively, and dichloromethane-d_2 was distilled from CaH_2. The electrochemical instrumentation, cells, data handling procedures, and electrodes have been previously described.[5a,24] Acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ was used as the solvent for electrochemical experiments and was passed through a column of active neutral alumina before use to remove water and protic impurities. The electrolyte was freed of air by purging with purified argon, and all measurements were carried out under a blanket of solvent-saturated argon at 293 K. ^1H NMR spectra were recorded on Varian XL-300 or Varian Gemini-200 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standard (δ 1.93 for acetonitrile, 5.32 for dichloromethane). Infrared spectra were obtained on a Perkin-Elmer 1310 infrared spectrophotometer. Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany. Compounds **1**,[25a] **2**,[6a] **3**,[25b] and **4**[11] were prepared according to published procedures.

$HRu(CO)(PPh_3)(NCMe)_3{}^+PF_6^-$ ((5)PF_6). A solution of **1** (50 mg, 0.109 mmol) in acetonitrile (20 mL) was treated with 75% aqueous HPF_6 (30 μL) while it was stirred vigorously at 0 °C for 30 min. The solvent was removed by vacuum transfer, and the residue was washed with ether. Recrystallization from acetonitrile/ether yielded (**5**)PF_6 (43 mg, 60%): white powder, mp 127–129 °C dec; ^1H NMR (dichloromethane-d_2) δ −13.70 (d, J_{P-H} = 23.9 Hz, 1 H), 1.89 (s, 3 H), 2.02 (br s, 3 H), 2.36 (s, 3 H), 7.4–7.6 (m, 15 H); IR (acetonitrile) ν_{CO} 1960 cm^{-1}. (Attempts at obtaining ^{13}C NMR spectra were frustrated by the gradual decomposition of the sample.) Anal. Calcd for $C_{25}H_{25}F_6N_3OP_2Ru$: C, 45.46; H, 3.81; N, 6.36. Found: C, 44.19; H, 4.31; N, 6.20.

$HRu(CO)(PPh_3)_2(NCMe)_2{}^+PF_6^-$ ((6)PF_6). This compound was prepared in a manner analogous to that reported for the corresponding perchlorate salt.[12] Thus, a yellow suspension of $HRu(CO)(PPh_3)_3Cl$[25c] (200 mg, 0.210 mmol) and KPF_6 (77.9 mg, 0.432 mmol) in acetonitrile (10 mL) was stirred for 12 h. The white precipitate was separated by decanting, and the supernatant was concentrated by rotary evaporation and dried in vacuo. The resulting white powder was washed repeatedly with ether and recrystallized from dichloromethane/ether, yielding the product (155 mg, 84%): white powder, mp 190–200 °C dec; ^1H NMR (dichloromethane-d_2) δ −13.02 (t, J = 18.1 Hz, 1 H), 1.32 (t, J = 1.4 Hz, 3 H), 1.80 (s, 3 H), 7.0–7.6 (m, 30 H); IR (acetonitrile) ν_{CO} 1955 cm^{-1}. Anal. Calcd for $C_{41}H_{37}F_6N_2OP_3Ru$: C, 55.85; H, 4.23; N, 3.18. Found: C, 56.65; H, 4.61; N, 3.74.

Reaction between Oxidatively Generated 5 and PPh_3. A mixture of **1** (6.0 mg, 0.0131 mmol) and **3** (4.2 mg, 0.0127 mmol) was dissolved in acetonitrile-d_3 (0.5 mL) in an NMR tube. The solution turned yellow upon the consumption of **3**. A ^1H NMR spectrum recorded at this point showed the presence of ferrocene, cyclopentadiene, **2**-d_3, **5**-d_9, and a trace of unreacted **1**. The NMR tube was opened in the drybox, PPh_3 (3.5 mg, 0.0133 mmol) was added, and a new ^1H NMR spectrum was recorded. The only change, except for subtle differences in the aromatic region, was that the hydride doublet due to **5**-d_9 (δ −13.77) had been replaced by the hydride triplet of $HRu(CO)(PPh_3)_2(NCCD_3)_2{}^+$ (**6**-d_6) (δ −13.05).

Preparative-Scale Oxidation of 1 with $(\eta^5\text{-}C_5H_5)Fe^+PF_6^-$ (3). To a solution of **1** (56 mg, 0.122 mmol) and 2,6-lutidine (30 μL, 0.257 mmol) in acetonitrile (20 mL) was added solid **3** (80

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[21] Abbreviations: dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dmpe = 1,2-bis(dimethylphosphino)ethane.

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mg, 0.242 mmol). The solution was stirred for 12 h at ambient temperature. The solvent was removed in vacuo, and ferrocene and the small excess of substrate were removed by washing the residue with ether on a medium-porosity-frit filter until the filtrate appeared colorless. The orange solid material was dissolved in dichloromethane (10 mL), and the solution was extracted with water (2 × 6 mL), dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. Recrystallization from dichloromethane/ether yielded **2** (49.3 mg, 63%), pure as judged by ^1H NMR and IR spectroscopy.

Oxidation of 1 with 3 in NMR Tubes. In all these experiments, **1** (4.0 mg, 0.0088 mmol), **3** (ca. 2.7 mg, 0.0083 mmol), and additional reagents (2,6-lutidine, $HBF_4 \cdot Et_2O$, aqueous HBF_4 or HPF_6, when applicable) were loaded into an NMR tube equipped with a ground-glass joint, and the tube was attached to the vacuum line. The solvent of choice (ca. 0.4 mL) was added by vacuum transfer, and the tube was sealed under vacuum and kept at liquid-nitrogen temperature until it was inserted in the NMR probe at the preselected temperature.

For determination of absolute yields and conversions of substrate with hexamethylbenzene (HMB) as an internal standard, the following procedure was employed. A mixture of **1** (8.0 mg, 0.0175 mmol) and HMB (ca. 0.9 mg, 0.0055 mmol) was dissolved in ether (1.0 mL). The solution was distributed equally into two separate NMR tubes, and the ether was carefully removed by vacuum transfer. The oxidizing agent (and, if applicable, other reagents) were added to one tube, which was sealed under vacuum after addition of the solvent. The other tube was sealed after the addition of solvent. The relative intensities of the substrate η^5-C_5H_5 signal and the HMB singlet provided a reference for the calculation of substrate conversion and product yields.

Constant-Current Coulometry and Preparative Electrolysis Experiments. Constant-current electrolyses with DCV monitoring of the disappearance of substrate were carried out in a H-shaped cell, the compartments of which were separated by a fritted-glass junction. A Pt-gauze working electrode was used. Solutions that contained 2.0–2.5 mM hydride **1** in 20 mL of acetonitrile/0.1 M $Bu_4N^+PF_6^-$ were electrolyzed with a constant current of 10 mA. The preparative electrolysis was carried out in acetonitrile/0.05 M $Me_4N^+PF_6^-$. A solution of **1** (41.3 mg, 0.090 mmol) in the electrolyte solution (20 mL) was electrolyzed for the time that was required for the passage of 2.0 faraday/mol of charge. The solution was concentrated by rotary evaporation, and the residue was extracted with dichloromethane (5 mL). The filtered extract was concentrated, and **2** (53.7 mg, 92.6%) was isolated as the only product after recrystallization from dichloromethane/ether. The product appeared pure by IR and ^1H NMR spectroscopy, and the spectra were identical with those of an authentic sample.[6a]

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Low-Valent, Heterobinuclear Complexes of Rhodium and Osmium. Influence of the Coordinatively Unsaturated Rhodium Center on the Reactivity

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The coordinatively unsaturated complex $[RhOsH(CO)_3(dppm)_2]$ (**1**) is converted smoothly to the chloro analogue $[RhOsCl(CO)_3(dppm)_2]$ (**2**) in carbon tetrachloride. Compound **1** also reacts with the electrophiles $HBF_4 \cdot Et_2O$ and $[AuPPh_3][BF_4]$, yielding $[RhOs(CO)_3(\mu\text{-}H)(\mu\text{-}X)(dppm)_2][BF_4]$ (X = H (**3**), $AuPPh_3$ (**4**)). The bridging $AuPPh_3$ group is readily replaced by an iodo group in the reaction of **4** with I_2, yielding $[RhOs(CO)_3(\mu\text{-}H)(\mu\text{-}I)(dppm)_2][BF_4]$ (**5**). Reductive elimination of H_2 from **3**, in the presence of carbon monoxide, is reversible and yields $[RhOs(CO)_4(dppm)_2][BF_4]$ (**6**), which also reacts with the above electrophiles, yielding $[RhOs(CO)_4(\mu\text{-}X)(dppm)_2][BF_4]_2$ (X = H (**7**), $AuPPh_3$ (**8**)). Reaction of **6** with ^tBuNC leads to substitution of the carbonyl on Os that is trans to the Rh–Os bond to give $[RhOs(CO)_3(^tBuNC)(dppm)_2][BF_4]$ (**9**). Compound **6** also reacts with the alkynes dimethyl acetylenedicarboxylate (DMAD) and hexafluoro-2-butyne (HFB) to give the alkyne-bridged products $[RhOs(CO)_3(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**11**) and $[RhOs(CO)_3(\mu\text{-}HFB)(dppm)_2][BF_4]$ (**13**), respectively. Carbonyl loss from **11** occurs under mild conditions to yield $[RhOs(CO)_3(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**12**), analogous to compound **13**. This carbonyl loss is facilitated by donation of a pair of electrons from Rh to Os with formation of a Rh→Os dative bond. Addition of anionic or neutral ligands (L) to compound **12** yields the species $[RhOs(CO)_2L(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2]^{n+}$ (n = 0, 1, respectively), in which L is coordinated on Rh and the original Rh-bound carbonyl has moved to the bridging site. Neutral ligands such as isocyanides react with **13** to yield products analogous to those obtained with **12**; however, the I^- and $S_2PMe_2^-$ anions (X^-) react with **12** with accompanying CO loss to yield $[RhOsX(CO)_2(\mu\text{-}HFB)(dppm)_2]$, in which X is bound to Rh with both carbonyls on Os. The other alkyne-bridged dicarbonyls $[RhOs(CO)_2L(\mu\text{-}RC{\equiv}CR)(dppm)_2]^{n+}$ can also be obtained by heating the tricarbonyl precursors. The structure of compound **12** has been determined by X-ray techniques. This compound crystallizes with two CH_2Cl_2 molecules in the triclinic space group $P\bar{1}$ with a = 14.811 (2) Å, b = 19.250 (3) Å, c = 11.611 (1) Å, α = 103.27 (1)°, β = 94.26 (1)°, γ = 87.74 (1)°, V = 3212 (2) Å^3, and Z = 2. Refinement has converged at R = 0.041 and R_w = 0.060 on the basis of 9594 unique observations and 512 parameters varied. The geometry about Rh is essentially square planar, ignoring the Rh–Os interaction, whereas that about Os is a distorted octahedron when the dative Rh→Os interaction is taken into account. The Rh–Os separation of 2.8744 (3) Å is consistent with a single bond.

Introduction

Interest in the organometallic chemistry of heterobinuclear complexes has arisen because of the possibility of unique chemistry resulting as a consequence of having two metals of different chemical properties in close mutual proximity[1] and also because of the related catalytic im-

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