in our laboratory to synthesize this reagent and to determine if a μ-CHO product will derive from it.

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Registry No. **1**, 89438-28-8; **3**, 89438-29-9; **4**, 89438-30-2; **5**, 89438-32-4; $MnH(CO)_3(PMePh_2)_2$, 42965-72-0; $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, 11117-09-2; $CH_3Mn(CO)_5$, 13601-24-6; $FeCp(PPh_2)(CO)_2$, 38816-40-9; $Mn_2(CO)_{10}$, 10170-69-1; $HMn(CO)_5$, 16972-33-1; MeLi, 917-54-4; $[Ph_3C]BF_4$, 341-02-6; HBF_4, 16872-11-0; $[(CH_3)_3O]BF_4$, 420-37-1; H_2, 1333-74-0; CO, 630-08-0.

Supplementary Material Available: Tables of positional and thermal parameters, bond lengths and angles, and structure factors for the X-ray crystallographic studies of 1 and 3 (41 pages). Ordering information is given on any current masthead page.

Acid–Base Chemistry of the Methylrhodium(III) Derivative $CH_3RhI_2(PPh_3)_2$

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Reaction of excess methyl iodide with the 14-electron Rh(I) salt $(Ph_3P)_3Rh^+HC(SO_2CF_3)_2^-$ produces green $CH_3RhI_2(PPh_3)_2$, λ_{max} 500 and 610 nm. Crystal data: monoclinic (centric), $C2/c$, a = 23.982 (5) Å, b = 9.828 (3) Å, c = 16.063 (6) Å, β = 114.73 (3)°, Z = 4, and V = 3439 (4) Å^3. The structure, solved by using 2618 reflections for which $F_o^2 > 1.0\ \sigma(F_o^2)$, converged at R = 0.022 and R_w = 0.034. The coordination geometry of rhodium(III) is flattened square pyramidal with a C_2 axis through rhodium and the methyl carbon. The metal is displaced 0.25 Å toward the apical methyl group from the least-squares plane containing two trans iodines and two trans phosphorus atoms, which comprise the base of the pyramid. Important bond distances are d(Rh–C) = 2.06 (1) Å, d(Rh–I) = 2.635 (1) Å, and d(Rh–P) = 2.365 (2) Å. $CH_3RhI_2(PPh_3)_2$ has an extensive acid–base chemistry. It is converted by excess carbon monoxide to *cis*- and *trans*-$CH_3CORhI_2(PPh_3)_2CO$ from which reversible dissociation of the terminal carbonyl ligand leads to $CH_3CORhI_2(PPh_3)_2$. This acetylrhodium(III) compound decomposes by reductive elimination of methyl iodide to form $(Ph_3P)_2Rh(CO)I$. Trimethylphosphine and trimethyl phosphite displace triphenylphosphine to yield *mer*-$CH_3RhI_2L_3$ (L = $(CH_3O)_3P$, $(CH_3)_3P$). Migratory insertion of sulfur dioxide into the CH_3 bond provides $CH_3SO_2RhI_2(PPh_3)_2$.

Introduction

During the course of a systematic examination of the chemistry of $(Ph_3P)_3Rh^+HC(SO_2CF_3)_2^-$, we found that this 14-electron rhodium(I) compound reacted with methyl iodide to form the methylrhodium(III) derivative $CH_3RhI_2(PPh_3)_2$.[1] Since alkylrhodium(III) materials are not common, a structural and chemical study was undertaken. The metal center behaves as a soft Lewis acid, and in this paper, we describe the acid–base chemistry of $CH_3RhI_2(PPh_3)_2$ as probed by vibrational and NMR spectroscopy.

Results

Reaction of $(Ph_3P)_3Rh^+HC(SO_2CF_3)_2^-$ with excess methyl iodide in dichloromethane at room temperature provides green crystals, compositionally defined by NMR data and elemental analyses as $CH_3RhI_2(PPh_3)_2$, 1, in 58% yield. Electronic and NMR spectra indicate that this material is similar to $CH_3RhI_2(PPh_3)_2{\cdot}CH_3I$ first described by Wilkinson and co-workers.[2] However, the nature of the "extra" methyl iodide in Wilkinson's compound remains unresolved and the only other reference to this curious substance is a report of its X-ray photoelectron spectrum.[3] In the ^1H NMR spectrum of 1, the protons of the methylrhodium group appear as a doublet of triplets, δ 2.86, with $^2J_{H\text{-}C\text{-}Rh}$ = 2.7 Hz and $^3J_{H\text{-}C\text{-}Rh\text{-}P}$ = 5.3 Hz. The three-bond coupling constant is twice that of the two-bond coupling, but a similar pattern has been noted in $CH_3Rh(PPh_3)_3$.[3] The ^{13}C NMR spectrum of $^{13}CH_3RhI_2(PPh_3)_2$, prepared from $(Ph_3P)_3Rh^+HC(SO_2CF_3)_2^-$ and 99 atom % $^{13}CH_3I$, reveals a multiplet at δ −3.2 for the methyl group with $^1J_{C\text{-}Rh}$ = 24.6 Hz, $^1J_{C\text{-}H}$ = 143 Hz, and $^2J_{C\text{-}Rh\text{-}P}$ = 5.9 Hz. The infrared spectrum (KBr disk) shows a sharp, weak band at 2910 cm^{-1} that is attributed to C–H stretching in the CH_3Rh unit. It is found at 2120 cm^{-1} in $CD_3RhI_2(PPh_3)_2$.

Structure of $CH_3RhI_2(PPh_3)_2$. The solid-state molecular structure of 1 is depicted in Figure 1. There are no unusually short intermolecular contacts. In general, the structure resembles that of a benzene solvate described in a preliminary communication by Skapski et al.[5] The

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[1] Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Howells, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1510.

[2] (a) Lawson, D. N.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1733. (b) Douek, I. C.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 2604.

[3] Hamer, A. D.; Tisley, D. G.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1973**, 116.

[4] Keim, W. *J. Organomet. Chem.* **1968**, *14*, 179.

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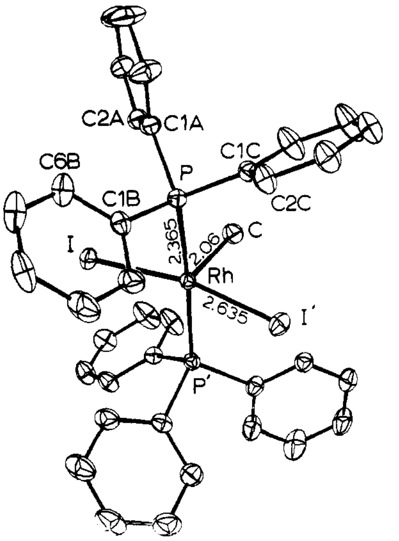

Figure 1. Molecular structure of $CH_3RhI_2(PPh_3)_2$. Ellipsoids are drawn with 30% probability surfaces. A crystallographic C_2 axis contains the Rh and C atoms and relates the primed to the unprimed atoms. Some angles within the coordination core are I–Rh–I′ = 164.47 (3)°, -P = 89.73 (3)°, -P′ = 89.33 (3)°, and -C = 97.77 (2)° and P–Rh–P′ = 173.04 (4)° and -C = 93.48 (3). The esd's in the last significant figure of the distances are for Rh–I(1), Rh–P(2), Rh–C(1).

molecule has crystallographic C_2 symmetry. The ligands about rhodium form a flattened square-based pyramid. The two phosphorus atoms are displaced upward toward the apical methyl group by 0.11 Å from the P_2I_2 least-squares plane and the two iodine atoms are displaced downward by the same amount. The central rhodium atom is displaced 0.25 Å out of the P_2I_2 plane in the direction of the methyl group. Important bond lengths and angles are given in Figure 1 and the atomic coordinates in Table S1. Tables of thermal parameters and calculated hydrogen positional parameters and structure factor amplitudes and an ORTEP stereoview of the molecule are available as Tables S2 and S3 and Figure S1, respectively.

Acid–Base Chemistry. Recrystallization from a benzene solution containing a large excess of dimethyl sulfide produces only the 1:1 benzene solvate of 1 rather than the 1:1 adduct anticipated for a Rh(III) acceptor. The carbonylation chemistry, however, is considerably more complicated than might have been anticipated from the literature[2a,b] and is summarized in Figure 2. Infrared and NMR analysis of solutions of 1 that have been treated with excess carbon monoxide at atmospheric pressure provides clear evidence for the formation of two new rhodium(III) species in a 2:1 ratio. The major component **2a** shows carbonyl stretching bands at 1962 and 1669 cm^{-1} and a peak in the ^1H NMR spectrum at 3.23 ppm. The compound formed in lesser amount, **2b**, has carbonyl stretching bands at 2080 and 1707 cm^{-1} and a ^1H resonance at 1.14 ppm. The lower frequency 1669 and 1707 cm^{-1} bands are clearly attributable to Rh–$COCH_3$ groups. In agreement with this, the 3.23 and 1.14 ppm peaks are sharp singlets that show no spin coupling to ^{31}P or ^{103}Rh. The higher frequency bands at 1962 and 2080 cm^{-1} are similarly attributable to C–O stretching in a terminal Rh–CO group. Thus, **2a** and **2b** are isomers of $CH_3CORhI_2(PPh_3)_2CO$. We propose that **2b** is the isomer in which the CH_3CO and Co ligands are cis to one another since, in this geometry, the methyl protons should experience shielding due to diamagnetic circulation of electrons in the C–O bond. If the two triphenylphosphine ligands are placed trans to one another to minimize nonbonded repulsions, then the plausible structure shown in Figure 2 follows. Likewise, **2a** is proposed to be *trans*-$CH_3CORhI_2(PPh_3)_2CO$, in which the acetyl and carbonyl groups are mutually trans. Both **2a** and **2b** have similar ^{31}P chemical shifts since the ^{31}P NMR spectrum of the mixture shows one doublet at 30.0 ppm (J_{RhP} = 84 Hz) and no evidence of free triphenylphosphine. Thus, phosphine equivalence reflects similar chemical environments in **2a** and **2b**, implicit in Figure 2, and not rapid phosphine dissociation.

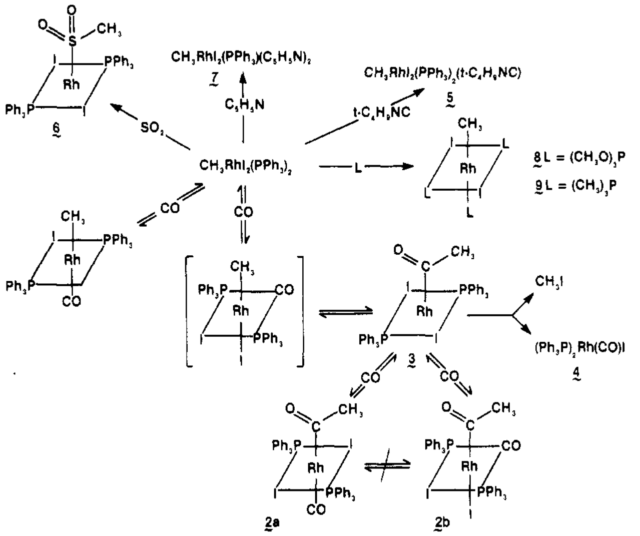

Figure 2. Acid–base chemistry of $CH_3RhI_2(PPh_3)_2$.

The cis isomer **2b** is less soluble than **2a** in dichloromethane–butanone, and when 1 is treated with excess carbon monoxide in this solvent mixture, **2b** crystallizes from the solution and may be isolated in analytically and spectroscopically pure form. In a potassium bromide disk, **2b** shows carbonyl absorptions at 2100 and 1705 cm^{-1}, in good agreement with the spectral features deduced from analysis of a mixture of **2a** and **2b**.

When solutions of *cis*- and *trans*-$CH_3CORhI_2(PPh_3)_2CO$ are purged for several minutes with nitrogen in order to displace carbon monoxide, evidence for rapid decomposition is dramatic. Fourier transform infrared analysis shows that the characteristic absorptions of **2a,b** at 1669, 1707, 1962, and 2080 cm^{-1} decrease to less than 25% of their original intensity. A new peak at 1711 cm^{-1}, assigned to $CH_3CORhI_2(PPh_3)_2$, **3**, grows in. NMR spectra show that **3** has $\delta(^1H)$ 2.83 (sharp singlet) and $\delta(^{31}P)$ 20.7 (d, J_{RhP} = 106 Hz); no free triphenylphosphine is produced. Proton NMR spectra show that **2b** decomposes about three times as rapidly as **2a**. Treatment of **3** with carbon monoxide regenerates *both* **2a** *and* **2b**. In a separate experiment, decarbonylation of the pure *cis* acetylrhodium carbonyl **2b** was found by ^1H NMR to produce **3** and none of trans isomer **2a**. Thus, **2a** and **2b** interconvert, not directly, but through five-coordinate acetylrhodium(III) species **3**, and the **2a**:**2b** ratio reflects relative thermodynamic stabilities. This acetylrhodium compound is itself unstable in solution. Decomposition in dichloromethane, monitored by FTIR and ^1H NMR spectroscopy, leads irreversibly to methyl iodide, δ 2.16, and $(Ph_3P)_2Rh(CO)I$, **4**, ν_{CO} 1983 cm^{-1}. The first-order rate constant for this process is 2.3 × 10^{-4} s at 27 °C. **4** is likely the trans isomer for which ν_{CO} 1981 cm^{-1} has been reported.[5] No evidence for the formation of acetyl iodide or acetic acid was found.

tert-Butyl isocyanide and 1 form a 1:1 complex, $CH_3Rh(t\text{-}C_4H_9NC)I_2(PPh_3)_2$, **5**, with ν_{NC} 2106 cm^{-1}. This

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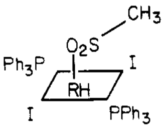
[5] Troughton, P. G. H.; Skapski, A. C. *Chem. Commun.* **1968**, 575.

[6] Collman, J. P.; Kubota, M.; Valentine, F. D.; Sui, J. Y.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430.

compound is stable in the solid state, but ^1H NMR spectra of chloroform solutions are indicative of facile decomposition, exhibiting a plethora of methyl proton resonances along with a singlet due to methyl iodide.

Migratory insertion occurs in the reaction of **1** with sulfur dioxide which generates $CH_3SO_2RhI_2(PPh_3)_2$, **6**. In this compound, the methyl proton resonance appears as a sharp singlet, δ 3.07, with no coupling to Rh or P observed; the ^{31}P NMR spectrum comprises a doublet, δ 16.7 (J_{RhP} = 102 Hz), indicating that the two triphenylphosphine ligands remain equivalent and cis to one another. The ν_2(S–O) antisymmetric stretch appears as a strong band at 1255 cm^{-1} (Nujol). Positive identification of the symmetric S–O band is difficult because of overlap with a 1090 cm^{-1} absorption of triphenylphosphine, but it may appear as a shoulder at 1085 cm^{-1} on this peak.[7] The spectroscopic data indicate that insertion of sulfur dioxide occurs without detectable rearrangement and that the product has the stereochemistry shown in **6**.



6

From **1** and excess pyridine (py) are obtained two isomers of $CH_3RhI_2(py)_2PPh_3$ in a 2.6:1 ratio. The major isomer **7a** has $\delta(^{31}P)$ 29.0 (J_{Rh-P} = 126 Hz) and $\delta(^1H)$ 2.42 (t, $^2J_{Rh-C-H} \simeq {^3J_{P-Rh-C-H}}$ = 2.3 Hz). For the minor isomer **7b**, $\delta(^{31}P)$ is 32.3 (J_{Rh-P} = 128 Hz) and $\delta(^1H)$ is 1.86 (t, J = 2.3 Hz). The NMR data at hand do not define the stereochemistries of **7a**,**b**, and we have been unable to separate completely the two isomers. A different reactivity pattern is observed for trimethyl phosphite and trimethylphosphine. These bases displace triphenylphosphine to form six-coordinate *mer*-$CH_3RhI_2L_3$ (L = $(CH_3O)_3P$, $(CH_3)_3P$). In $CH_3RhI_2[P(OMe)_3]_3$, **8**, the ^{31}P NMR spectrum displays the A_2B portion of an A_2BX pattern with $\delta(P_a)$ 106.9, $\delta(P_b)$ 104.6, J_{PaPb} = 36 Hz, J_{PaRh} = 152 Hz, and J_{PbRh} = 211 Hz. The chemical shifts and coupling constants in this non-first-order spectrum were determined by comparison with a calculated spectrum. The ^{31}P NMR data are consistent with a proposed structure for **8** by replacement of both Ph_3P ligands by $(MeO)_3P$ and coordination of an additional trimethyl phosphite to the vacant position trans to the methyl group. In accord with this structure, the ^1H NMR spectrum reveals two types of $(MeO)_3P$ ligands in a 2:1 ratio. The methoxy groups of the mutually trans phosphite groups exhibit virtual coupling to the ^{31}P and give rise to a triplet at 3.89 ppm with 5.3-Hz splitting; methyl protons in the unique trimethyl phosphite ligand appear as a doublet at 3.82 ppm with 10.6-Hz coupling. The CH_3Rh protons give rise to a multiplet at 1.56 ppm.

Treatment of **1** with excess trimethylphosphine similarly affords *mer*-$CH_3RhI_2[P(CH_3)_3]_3$, **9**, whose structure is analogous to that proposed for **8**. Two equivalent $(CH_3)_3P$ groups give rise to a doublet of doublets in the ^{31}P NMR spectrum at δ – 23.0 (J_{P-Rh} = 92 Hz, J_{PaPb} = 24 Hz), while the unique trimethylphosphine trans to the methyl group gives rise to a doublet of triplets at δ – 41.1 (J_{P-Rh} = 79 Hz, J_{PP} = 25 Hz). Again, virtual coupling, due to the large trans P–P spin interaction in the pair of equivalent $(CH_3)_3P$ donors leads to a triplet pattern in the ^1H NMR spectrum at 1.76 ppm (3.1-Hz splitting); the protons of the unique $(CH_3)_3P$ ligand are associated with a 6.9-Hz doublet at 1.62 ppm. The CH_3–Rh protons appear as a doublet of quartets, δ 1.07, with $^2J_{RH-C-H}$ = 1.7 Hz and $^3J_{P-Rh-C-H}$ = 6.0 Hz. Since the ^{31}P NMR spectrum of **9** was first order and readily interpretable, the ^{13}C analogue, $^{13}CH_3RhI_2[P(CH_3)_3]_3$, was prepared from $^{13}CH_3RhI_2(PPh_3)_2$ in order to definitively establish by ^{13}C NMR spectroscopy the stereochemistry of **9**. In the $^{13}C\{^1H\}$ NMR spectrum of this labeled derivative, the methylrhodium carbon appears at δ –6.3. The resonance is a doublet of triplets of doublets with $^1J_{Rh-C}$ = 104 Hz, $^2J_{P-C}$ = 8.0 Hz (triplet), and $^2J_{P-C}$ = 14.1 Hz (doublet). From the undecoupled spectrum, J_{C-H} is found to be 132 Hz. These data strongly support the proposed structure for **9**: the two equivalent equatorial $(CH_3)_3P$ ligands are cis to the $^{13}CH_3$ group and give rise to the 8.0-Hz triplet splitting. The single trans axial $(CH_3)_3P$ ligand provides, as expected, the larger, 14.1 Hz, two-bond P–Rh–C coupling.

Discussion

The acid–base chemistry of $CH_3RhI_2(PPh_3)_2$ appears to be quite extensive. Carbonylation reactions in particular are unexpectedly complex. With excess carbon monoxide, two isomers of $CH_3CORhI_2(PPh_3)_2CO$ are obtained. The major isomer **2a** has ν_{CO} 1962 and 1669 cm^{-1} and $\delta(^1H)$ 3.23. The minor isomer **2b** has ν_{CO} 2080 and 1707 cm^{-1} and $\delta(^1H)$ 1.14. Assignments to **2a**,**b** are made on the basis of the relative intensities of the various spectral features and not from preconceived expectations of peak positions. The ^1H spectra of both species show sharp singlets showing no indication of spin coupling to ^{31}P or ^{103}Rh. This provides strong evidence that **2a**,**b** are indeed acetylrhodium carbonyl complexes although Wilkinson et al.[2] obtained from $CH_3RhI_2(PPh_3)_2{\cdot}CH_3I$ and carbon monoxide a material having ν_{CO} 2040 cm^{-1} which was formulated as $CH_3RhI_2(PPh_3)_2CO$. The nature of the initial reaction product containing only 1 equiv of carbon monoxide is not easily resolved because reversible uptake of a second equivalent of carbon monoxide is sufficiently rapid that pure samples of the monocarbonyl complex have not been isolated. Douek and Wilkinson[2b] have obtained kinetic evidence for the intermediacy of a methylrhodium species and for the formation of **3** from **2**, but in contrast with our results, these workers attributed 2075 and 1680 cm^{-1} bands to a unique but stereochemically undefined isomer of **2**. A further difficulty is introduced by the instability of the monocarbonyl species toward reductive elimination (vide infra). We have approached this question by examining the infrared and ^1H NMR spectra of solutions of $CH_3CORhI_2(PPh_3)_2$ in dichloromethane which have been purged with nitrogen, this step serving to displace carbon monoxide and to generate the monocarbonyl compound. In such solutions, a sharp singlet at 2.83 ppm and a strong acetyl CO stretching band at 1711 cm^{-1} are apparent and these spectra features are assigned to the acetylrhodium derivative $CH_3CORhI_2(PPh_3)_2$, **3**. There is no spectroscopic evidence for the presence of $CH_3RhI_2(PPh_3)_2CO$. It thus appears that coordination of carbon monoxide to **1** is followed by rapid migratory insertion to form the acetyl derivative **3** and, indeed, a similar rapid insertion reaction involving sulfur dioxide produces $CH_3SO_2RhI_2(PPh_3)_2$, **6**, and no spectroscopically detectable interme-

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[7] The usual range for ν_{as} is 1250–1100 cm^{-1} and for ν_s, 1100–1000 cm^{-1} in (alkylsulfonyl)metal compounds. See: Wojcicki, A. *Adv. Organomet. Chem.* 1974, *12*, 31.

[8] Carbonylation of 1 is similar in some respects to that involved in the rhodium- and iodine-catalyzed carbonylation of methanol to produce acetic acid which involves sequentially $Rh(CO)_2I_2^-$, $CH_3Rh(CO)_2I_3^-$, $CH_3CORh(CO)I_3^-$, and $CH_3CORh(CO)_2I_3^-$. Reductive elimination of CH_3COI occurs from the latter compound: Intille, G. M. *Inorg. Chem.* 1972, *11*, 695.

[9] Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; p 80.

diate. Details of the mechanism(s) by which **3** and **6** arise remain unclear. Examination of the structure of **1** suggests that initial coordination of small donor molecules should occur by attack at the relatively unhindered axial position opposite the methyl group. This, however, would generate trans adducts, and it is currently considered that migratory insertion reactions require a cis orientation of the reacting groups. Therefore, attack may also occur at one of the triangular faces, the corners of which are comprised by CH_3, I, and Ph_3P groups, of square-pyramidal $CH_3RhI_2(PPh_3)_2$ to generate *cis*-$CH_3RhI_2(PPh_3)_2$(donor). In the case of carbon monoxide, we suggest that attack occurs at a triangular face to produce as a kinetically unstable intermediate *cis*-$CH_3RhI_2(PPh_3)_2CO$ which undergoes facile insertion of CO into the cis CH_3–Rh bond to form $(CH_3CO)RhI_2(PPh_3)_2$, **3**. Equilibrium loss of carbon monoxide provides a pathway for cis–trans isomerization. Carbonyl lability in **2a**,**b** is indicated by the ^{13}C NMR spectra of these materials, prepared from **1** and 90 atom % ^{13}CO, which displays a broad singlet at δ 189.5 ($W/2$ = 30 Hz). In **2a**,**b**, there appears to be little or no tendency for reductive elimination to occur until the terminal carbonyl ligand is removed, whereupon methyl iodide rather than acetyl iodide is lost.

The ratio of the relative rates of decomposition of **2a** and **2b**, determined by ^1H NMR, is 1:3. The lower stability of the cis isomer **2b** can be rationalized by an equilibrium loss of carbon monoxide, followed by a retroinsertion to reform a CH_3–Rh bond and then elimination of the cis CH_3 and I groups as methyl iodide. The methyl group enters the position formerly occupied by the departed cis carbonyl ligand, a pathway which is not available to the trans isomer **2a**.

Formation of methyl iodide from complexes of $CH_3RhI_2(PPh_3)_2$ is observed only when a strong π-acceptor ligand, such as carbon monoxide and *tert*-butyl isocyanide, is bonded to Rh(III). Ligands that are good σ donors and weaker π acceptors such as pyridine, trimethyl phosphite, and trimethylphosphine yield the adducts **7**, **8**, and **9** which show no tendency to reductive elimination of methyl iodide. Operationally, this imples that the better π acceptors favor reductive elimination by stabilizing, through increased back-bonding, the lower valent Rh(I) products.

Experimental Section

^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Varian XL-200 spectrometer and referenced respectively to internal $(CH_3)_4Si$ and external 85% H_3PO_4. Positive chemical shifts are downfield for all three nuclei. Infrared spectra of solids were obtained on Nujol mulls with a Perkin-Elmer 283 spectrometer while those of solutions were recorded on a Nicolet 7199 Fourier transform interferrometer. Peak positions obtained with these two instruments are considered to be accurate to within ±5 and ±1 cm^{-1}, respectively. A listing of infrared spectral data is given in Table S4.

$CH_3RhI_2(PPh_3)_2$, 1. With use of a vacuum line, 15 ml of dichloromethane and 0.4 ml of methyl iodide were condensed onto 1.2 g of $(Ph_3P)_3Rh^+HC(SO_2CF_3)_2^-$. The reaction mixture was warmed to room temperature and stirred for 3 h. Volatiles were removed by pumping, and the residue was twice recrystallized in air by slow rotary evaporation of a butanone–dichloromethane solution to provide 0.52 g (58%) of **1** as deep green needles: electronic spectrum (CH_2Cl_2) λ_{max} (log ϵ) 250 (sh), 340 (3.71), 500 (sh), 610 (2.31) nm; Raman spectrum (5144-Å excitation) $\Delta\nu$ 250, 290, 620, 685, 1000 (s), 1080, 1180, 1600, 3040 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.63 (m, H_o), 7.39 (m, $H_{m,p}$), 2.86 (dt, J = 2.9, 5.3 Hz); ^{13}C NMR (CD_2Cl_2) δ 128.1 (C_m, J_{PC} = 5.0 Hz), 130.3 (C_p), 132.9 (C_{ipso}, J_{PC} = 23 Hz), 135.1 (C_o, J_{PC} = 5.5 Hz). ^{13}C NMR data for the Rh–CH_3 group (see text) was obtained by using a sample of **1** prepared from 99 atom % $^{13}CH_3I$; the CD_3 analogue of **1** was also made by using CD_3I instead of CH_3I. Anal. Calcd for $C_{37}H_{33}I_2P_2Rh$: C, 49.6; H, 3.7; I, 28.4, Rh, 11.5; mol wt, 896. Found: C, 49.5; H, 3.9; I, 26.9; Rh, 11.5; mol wt, 874 (vapor pressure osmometry in $CHCl_3$).

***cis*-$CH_3CORhI_2(PPh_3)_2CO$, 2b.** Carbon monoxide was passed through a solution of 0.20 g of **1** in 8 mL of CH_2Cl_2 until a clear, homogeneous yellow-orange solution was obtained. Butanone, 5 mL, was added. Concentration of the reaction mixture under a stream of carbon monoxide afforded **2b** as gold-orange needles. These were collected on a filter, briefly vacuum dried, and stored at −20 °C. The yield was 0.12 g. Anal. Calcd for $C_{39}H_{33}I_2O_2P_2Rh$: C, 49.2; H, 3.5. Found: C, 49.1; H, 3.6.

$CH_3RhI_2(PPh_3)_2$(*t*-C_4H_9NC), 5. To 0.15 g (0.17 mmol) of **1** in 10 mL of cold (0 °C) dichloromethane was added three drops of *tert*-butyl isocyanide. Cold 2-propanol was added and the resulting orange solution quickly concentrated under vacuum to produce 0.1 g (60%) of golden microcrystals. After being vacuum dried, the compound was stored at −20° C. Anal. Calcd for $C_{42}H_{41}I_2NP_2Rh$: C, 51.5; H, 4.2; N, 1.4. Found: C, 50.8; H, 4.2; N, 1.4.

$CH_3SO_2RhI_2(PPh_3)_2$, 6. Sulfur dioxide was slowly passed through a stirred suspension of 0.2 g (0.22 mmol) of $CH_3RhI_2(PPh_3)_2$ in 12 mL of nitrogen-saturated benzene. After 20 min, the green starting material had been consumed and a yellow solution was obtained. *n*-Octane was added to the cloud point. The solution was then filtered and concentrated on a rotary evaporator to provide 0.15 g (71%) of **6** as small, yellow-brown crystals: electronic spectrum ($CHCl_3$) λ_{max} (log ϵ) 270 (4.32) nm. Anal. Calcd for $C_{37}H_{33}I_2O_2P_2RhS$: C, 46.3; H, 3.4; S, 3.2. Found: C, 46.8; H, 3.5; S, 3.2.

$CH_3RhI_2(PPh_3)(C_5H_5N)_2$, 7. Four drops of pyridine were added to 0.12 g (0.13 mmol) of **1** in 10 mL of dichloromethane. Ethanol, 3 mL, was added and the orange solution concentrated under reduced pressure to give 0.08 g (78%) of the pyridine complex as an orange powder: electronic spectrum (CH_2Cl_2) λ_{max} 350 (sh) nm. Anal. Calcd for $C_{29}H_{28}I_2N_2PRh$: C, 43.8; H, 3.5; N, 3.5. Found: C, 43.6; H, 3.5; N, 3.5.

$CH_3RhI_2[P(OMe)_3]_3$, 8. A suspension of 0.2 g (0.22 mmol) of **1** in 12 mL of toluene containing 0.2 mL of trimethyl phosphite was stirred for 20 min and then filtered. Volatiles were removed from the filtrate on a vacuum line, and the residue was extracted with three 20-mL portions of hot hexane. Recrystallization of the insoluble material by vacuum evaporation of a dichlormethane–hexane solution gave 0.08 g (49%) of **8** as a yellow powder. Anal. Calcd for $C_{10}H_{30}I_2O_9P_3Rh$: C, 16.1; H, 4.3. Found: C, 16.3; H, 4.2.

$CH_3RhI_2[P(CH_3)_3]_3$, 9. With use of a vacuum line, excess trimethylphosphine was condensed onto 0.18 g (0.20 mmol) of **1**. On thawing, the reaction mixture turned orange. Volatiles were pumped into a liquid-nitrogen-cooled trap. Two recrystallizations of the residue by slow concentration of a dichloromethane–hexane solution yielded 0.08 g (67%) of **9** as orange microcrystals: electronic spectrum (CH_2Cl_2) λ_{max} (log ϵ) 246 (4.39), 350 (3.41) nm. Anal. Calcd for $C_{10}H_{30}I_2P_3Rh$: C, 20.0; H, 5.0. Found: C, 20.4; H, 5.2.

Collection and Reduction of X-ray Data. A summary of crystal and intensity data for $CH_3RhI_2(PPh_3)_2$ is presented in Table S6. A crystal, grown by slow evaporation of a dichloromethane–toluene solution, was secured to the end of a glass fiber with 5-min epoxy resin. The crystal class was determined by use of the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs.[10] Background counts were measured at both ends of the scan range with the use of an ω–2θ scan, equal, at each side, to one-fourth of the scan range of the peak. In this manner, the total duration of background measurement is equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and no decay with time was noted. The data were corrected for Lorentz, polarization, and background effects. An empirical

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(10) All calculations were carried out on PDP 8A and 11/34 computers with use of the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described by: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Also: "CAD 4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, 1978.

absorption correction was applied by use of psi scan data and programs PSI and EAC.[10]

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom techniques. The Rh and I atoms were located by Patterson syntheses. Full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining non-hydrogen atoms. The atomic scattering factors were taken from the usual tabulation,[11] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers'[12] values of $\Delta f'$ and $\Delta f''$. Tables of observed and calculated structure factor amplitudes are available.[13] Hydrogen atom positions were calculated (C–H distance set at 0.95 Å) for all phenyl ring hydrogen atoms and were included in structure factor calculations but were not refined.

The methyl hydrogen atom positions were located by difference Fourier analysis and were found to be rotationally disordered about the crystallographic twofold axis that contains Rh and C. The final model included six methyl hydrogen positions.

The final difference Fourier map did not reveal chemically significant residual electron density. The final positional and thermal parameters of the refined atoms appear in Tables S1–S3.[13] The labeling scheme is presented in Figure 1.

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Supplementary Material Available: Tables of positional and thermal parameters, calculated hydrogen positional parameters, and observed and calculated structure factors and an ORTEP stereoview (19 pages). Ordering information is given on any current masthead page.

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[11] Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T. *Ibid.*; Table 2.3.1.

[12] Cromer, D. T.; Ibers J. A., in ref 11.

[13] See paragraph at end of paper regarding supplementary material.

Cryochemical Studies. 11. ESR Studies of the Reaction of Group 1B Metal Atoms with Some Mono- and Disubstituted Acetylenes in a Rotating Cryostat[1]

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Group 1B metal atoms have been deposited into inert hydrocarbon matrices with a variety of mono- and disubstituted alkynes at 77 K in a rotating cryostat, and their electron spin resonance spectra have been examined. The spectra show that the metal atoms react with the alkynes to give a variety of metal atom mono- and diligand complexes, ML and ML_2, and cis and trans organometallic vinyls. The ESR parameters for the complexes given by substituted alkynes are very similar to those for the prototype complexes $Cu[C_2H_2]$ and $Cu[C_2H_2]_2$ which suggests similar bonding and singly occupied molecular orbitals for all the species. Ab initio calculations have been performed on $Cu[C_2H_2]$ and $Cu[C_2H_2]_2$ and support the Dewar–Chatt–Duncanson model of metal–acetylene bonding. Metal and hydrogen hyperfine interactions for the organometallic vinyls show small differences depending on the nature of the alkyne.

Introduction

Several recent low-temperature (4–77 K) matrix isolation electron spin resonance spectroscopic (ESR) studies have shown that Cu atoms react with acetylene to give the mono- and diligand complexes $Cu[C_2H_2]$ and $Cu[C_2H_2]_2$,[3,4] that Ag atoms and acetylene give pseudocomplexes with one, two, three, and more than three ligands, $Ag\cdots(C_2H_2)$, $Ag\cdots(C_2H_2)_2$, and $Ag\cdots(C_2H_2)_{n\geq 3}$,[3] and the β-silver vinyl $AgCH{=}\dot{C}H$,[3,4] and that gold atoms and acetylene give the monoligand complex $Au[C_2H_2]$[5] and the vinyl and vinylidene radicals $AuCH{=}\dot{C}H$ and $Au\dot{C}{=}CH_2$.[4,5] Reaction of all three group 1B metal atoms with phenylacetylene give β-substituted α-styryls.[4]

Apart from our work on phenylacetylene very little is known about the paramagnetic properties of the species formed by reaction of metal atoms with substituted acetylenes. We, therefore, report here the results of a study of the reaction of a series of mono- and disubstituted acetylenes with the group 1B metal atoms Cu, Ag, and Au

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[1] (a) Issued as NRCC No. 23105. (b) Part 10. See: Howard, J. A.; Sutcliffe, R.; Mile, B. *J. Phys. Chem.* **1984**, *88*, 171–174.

[2] NRCC Research Associate.

[3] Kasai, P. H.; McLeod, D., Jr.; Watanabe, T. *J. Am. Chem. Soc.* **1980**, *102*, 179–190.

[4] Chenier, J. H. B.; Howard, J. A.; Mile, B.; Sutcliffe, R. *J. Am. Chem. Soc.* **1983**, *105*, 788–791.

[5] Kasai, P. H. *J. Am. Chem. Soc.* **1983**, *105*, 6704–6710.

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