Inorg. Chem. **1988**, *27*, 2473-2478

Almost invariably $g_\perp$ and $g_\perp'$ are broadened (variously ascribed to unresolved hyperfine splitting or g strain), and this contrasts with the situation for **1a–c** (but not **1d** and **1e**), where the lines are comparatively sharp.

In other recent studies we have identified further examples of paramagnetic *NCN′* metal complexes, i.e. [FeCl$_2$(*NCN′*)][17] (SP, high-spin) and [CoX(*NCN′*)L][32] (SP, low-spin). The Co(II) species, which have ESR data comparable to those of **1a–c**, were principally identified on the basis of spectroscopic (ESR, UV) measurements, and the relevant d-orbital ordering in Ni(III) and Co(II) d^7 species of *NCN′* has been fully described.[32]

Nickel Hydrogenases. It is now well established that certain hydrogenases contain a nickel center that in its oxidized form is a low-spin Ni(III) d^7 ion that gives rise to rhombic ESR spectra. There is evidence that one or more sulfur atoms are in the ligand sphere, and there is continuing research into the identification of the other ligating atoms and the metal geometry. Significantly, the g values of **1a–c** not only are similar to those obtained from the hydrogenases but also, unlike the situation with the Ni(III) peptide complexes, have comparably narrow line widths. This information together with the firmly established structure of **1c** makes these novel organometallic species an important reference point when one postulates and tests possible structures for the enzyme centers. In particular, **1a–c** show that it is possible with the appropriate geometry to have N donors present without necessarily producing broad ESR signals. Secondly, they show that a nickel center with a square-pyramidal array, i.e. with a vacant coordination site, could be the active center in the hydrogenase enzymes. Finally, since the value of the Ni^{2+}/Ni^{3+} redox couple of = +0.14 V vs SCE for the aquated [Ni(*NCN′*)] system is low compared to most other inorganic systems (including the peptide complexes), it can be inferred that oxygen (and hence sulfur) donors must be important in the hydrogenases,[33] where the value of this couple is typically −0.2 V (vs SHE).

Conclusions

The Ni(III) state, an electronic configuration which had hitherto been associated primarily with inorganic and coordination complexes, has now been shown to be a stable and readily accessible oxidation state in true organonickel species. The structural characterization of five-coordinate [Ni(*NCN′*)I$_2$], confirming a direct Ni–C bond, when combined with spectroscopic, conductivity, and electrochemical evidence adds a new dimension to the discussions regarding the nature, stability, and occurrence of tervalent nickel in organic and bioinorganic systems.

Acknowledgment. Dr. S. P. J. Albracht is thanked for many helpful discussions and for the measurement of Q-band ESR spectra.

Registry No. **1a**, 84500-90-3; **1b**, 84520-52-5; **1c**, 84500-91-4; **1d**, 84500-92-5; **1e**, 84500-93-6; **2a**, 84500-94-7; **2b**, 99532-40-8; **2c**, 99532-41-9; **2d**, 89618-54-2.

Supplementary Material Available: For **1c**, Tables II and V, listing anisotropic thermal parameters and least-squares planes, and Figure 3, showing a packing diagram of the unit cell, and for **1d** and **1e**, Figure 5, showing 9.50-GHz X-band ESR spectra of [Ni^{III}(*NCN′*)X$_2$] species in diglyme at ~150 K in the presence of added KX (4 pages); Table III, listing observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(31) (a) Lappin, A. G.; Murray, C. K.; Margerum, D. W. *Inorg. Chem.* **1978**, *17*, 1630–1634. (b) Sugiura, Y.; Mino, Y. *Inorg. Chem.* **1979**, *18*, 1336–1339. (c) Sugiura, Y.; Kuwahara, J.; Suzuki, T. *Biochem. Biophys. Res. Commun.* **1983**, *115*, 878–881.

(32) Van der Zeijden, A. A. H.; Van Koten, G. *Inorg. Chem.* **1986**, *25*, 4723–4725.

(33) Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2674–2876.

Contribution from 3M Corporate Research Laboratories
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Protonation of Cobalt, Rhodium, and Iridium Hydrides with Fluorocarbon Acids. Synthesis, Reactivity, and Dynamic Properties of $(Ph_3P)_3Rh^+$ and Its Derivatives

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Protonation of a variety of Co, Rh, and Ir hydrides with the fluorocarbon acids $H_2C(SO_2CF_3)_2$, $PhCH(SO_2CF_3)_2$, $HN(SO_2CF_3)_2$, $H_2C(SO_2C_8F_{17})_2$, and $C_8F_{17}SO_3H$ is reported. The Co and Ir hydrides form cationic dihydrides. Protonation of $(Ph_3P)_4RhH$ affords $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$. The stereochemical nonrigidity of $[(Ph_3P)_3Rh]^+$ in solution has been characterized by ^{31}P DNMR. Reactions of this 14-electron Rh(I) compound are described, including the solid-state carbonylation to yield $[(Ph_3P)_3Rh(CO)_2][HC(SO_2CF_3)_2]$. Carbon monoxide in the dicarbonyl salt is labile, and it dissociates in solution to give $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$. Fluorocarbon acids having long-chain perfluoroalkyl groups are useful in synthesizing salts that have high solubility in aromatic hydrocarbons.

Introduction

Reactions of protons with transition-metal hydrides are of considerable fundamental importance in organometallic and catalytic chemistry. Idealized protonation of such hydrides, M–H, represented by eq 1, can occur in ion cyclotron resonance ex-

$$M{-}H + H^+ \rightarrow MH_2^+ \rightarrow M^+ + H_2 \qquad (1)$$

periments[1] but are infrequently observed in fluid solution[2] because MH_2^+ and coordinatively unsaturated M^+ species tend to interact strongly with both counterions and nucleophilic solvents. Our approach to the study of inorganic proton-transfer reactions involves the use of bis((perfluoroalkyl)sulfonyl)alkanes in hydrocarbon solvents.[3-8] These fluorocarbon acids, of which $H_2C(SO_2CF_3)_2$ (**1**) and $PhCH(SO_2CF_3)_2$ (**2**) are exemplary, possess an unusual constellation of properties. They are strong, carbon-centered protic acids that are nonoxidizing, nonhygroscopic, and soluble in noncoordinating solvents such as toluene and di-

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[†] 3M Corporate Research Laboratories.

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(1) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967.

(2) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978.

(3) An alternate strategy utilizes neat CF_3SO_3H as both proton source and solvent. In this way, coordinatively unsaturated $Mn(CO)_5^+$ has been obtained: Trogler, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 6459.

(4) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Howells, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1510.

(5) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Organometallics* **1984**, *3*, 855.

(6) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Wang, D. X.; Albright, T. A. *Organometallics* **1986**, *5*, 38.

(7) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *24*, 1345.

(8) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 3412.

0020-1669/88/1327-2473$01.50/0

chloromethane. Their conjugate bases are highly sterically hindered, and only three examples have been found in which coordination to a metal, through a $Pt^{II}-C$ bond, have been encountered.[9,10] This paper presents a survey of the protonation chemistry of phosphine-substituted hydrides and carbonyl hydrides of the group VIII metals Co(I), Rh(I), and Ir(I). In particular, we shall examine the carbonylation reactions and dynamic properties of the 14-electron Rh(I) cation $[(Ph_3P)_3Rh]^+$.[11]

Results and Discussion

Protonation of Cobalt(I) and Iridium(I) Hydrides. The general technique used in protonation reactions consist of combining the organometallic hydride with an equimolar amount of **1** or **2** in deoxygenated toluene at room temperature. The resulting cationic hydrides, being saltlike, usually precipitate in analytically pure form and are isolated simply by filtration. The hydrides of both these group VIII metals react with bis((trifluoromethyl)-sulfonyl)alkanes by simple proton transfer (or oxidative addition), and the resulting dihydride species are readily isolable. Thus, reaction of red $(Ph_2PC_2H_4PPh_2)_2CoH$ or $(Ph_2PCH{=}CHPPh_2)_2CoH$ with **1** in toluene affords the yellow ionic compounds $[(Ph_2PC_2H_4PPh_2)_2CoH_2][HC(SO_2CF_3)_2]$ (**3**) and $[(Ph_2PCH{=}CHPPh_2)_2CoH_2][HC(SO_2CF_3)_2]$ (**4**), respectively. A cis stereochemistry for **3** is indicated by the appearance at 1965 and 1935 cm^{-1} of two Co–H stretching bands, which are at considerably higher frequency than in the starting materials, 1835 cm^{-1}, in agreement with the results of Sacco and Ugo for $[(Ph_2PC_2H_4PPh_2)_2CoH_2][ClO_4]$.[12] The ^1H NMR spectrum in CD_2Cl_2 between −30 and −70 °C demonstrates a broad resonance at −13.3 ppm integrated for two protons and a singlet at 3.85 ppm for the $HC(SO_2CF_3)_2^-$ anion. Similarly, **4** has ν_{CoH} at 1965 and 1940 cm^{-1} and a hydride resonance at −13.5 ppm. Solutions of **3** and **4** in dichloromethane, the only effective solvent found for NMR experiments, are thermally unstable, turning from yellow to green near room temperature and then giving rise to very broad ^1H NMR signals. Interestingly, no reaction between **1** and $[(PhO)_3P]_4CoH$ in toluene occurs up to 85 °C despite the fact that (trialkyl phosphite)cobalt(I) hydrides undergo facile protonation to yield *cis*-$[(RO)_3P]_4CoH_2^+$ complexes.[2] In this regard, Gosser[13] found that hydrogen chloride reacted readily with $[(PhO)_3P]_3CoH(CH_3CN)$ to form $[(PhO)_3P]_4CoCl$ while $[(PhO)_3P]_4CoH$ was inert and surmised that the reaction involved addition of HCl to the coordinatively unsaturated $[(PhO)_3P]_3CoH$ produced by dissociation of acetonitrile rather than attack on the hydride bound to cobalt. This cogent suggestion underscores the need for more detailed investigation of the mechanisms of organometallic proton-transfer processes.

Protonation of $(Ph_2PC_2H_4PPh_2)_2IrH$ with **1** affords [*cis*-$(Ph_2PC_2H_4PPh_2)_2IrH_2][HC(SO_2CF_3)_2]$ (**5**), with ν_{IrH} 2080 and 2060 cm^{-1} (cf. 2016 cm^{-1} in the neutral hydride).[13] The high-field portion of the ^1H NMR spectrum of this salt in CD_2Cl_2 solution, which has not been completely analyzed, is the AA′ portion of an AA′MM′XX′ pattern, centered at −11.7 ppm, from which only the trans P–H coupling, 114 Hz, has been unambiguously extracted. In tetrachloroethane, the ^1H NMR spectrum is unchanged up to 80 °C, at which temperature significant amounts of $[(Ph_2PC_2H_4PPh_2)_2IrHCl]^+$ begin to form. It thus appears that the octahedral Ir(III) species $[(Ph_2PC_2H_4PPh_2)_2IrX_2]^+$ (X = H, Cl) are stereochemically rigid whereas the hydrido chloride $[(Ph_2PC_2H_4PPh_2)_2IrHCl]^+$ is fluxional at room temperature.[14]

Protonation of $(Ph_3P)_3Ir(CO)H$ with **1** produces $[(Ph_3P)_3Ir(CO)H_2][HC(SO_2CF_3)_2]$ (**6**), with $\delta^{31}P$ 2.2 (d, 2 P) and 0.5 (t, 1 P, J_{PP} = 14 Hz) and $\delta^{19}F$ 81.6. In the 200-MHz ^1H NMR spectrum, the equatorial hydride, H_e, appears as a doublet of triplets of doublets at δ −11.4 with J_{H_eP2} = 114 Hz (d), $J_{H_eP1,3}$ = 18 Hz (t), and $J_{H_aH_e}$ = 4 Hz (d). The axial proton (H_a) resonance, δ −9.6, is a triplet of doublets of doublets with $J_{H_aP1,3}$ = 19 Hz and J_{H_aP2} = 13 Hz, in substantial agreement with the data reported for the crystallographically characterized $[SiF_5]^-$ salt.[15]

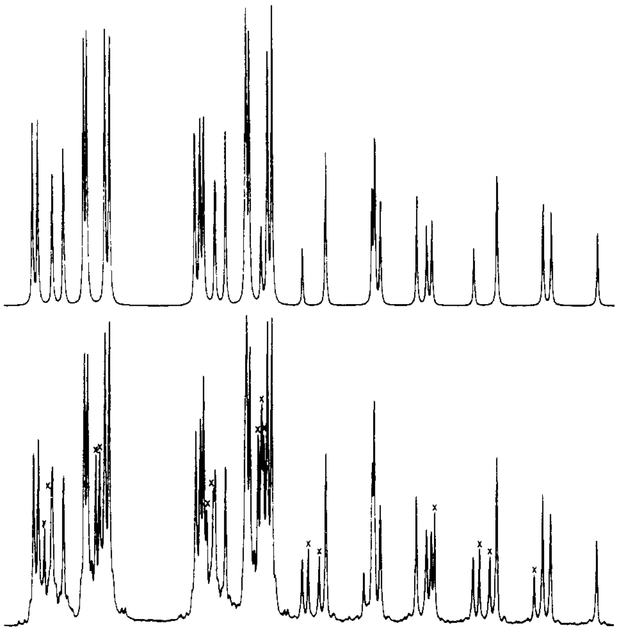

Figure 1. Calculated (upper) and observed (lower) $^{31}P\{^1H\}$ NMR spectra of $[(Ph_3P)_3Rh(^{13}CO)][HC(SO_2CF_3)_2]$. Peaks marked × in the experimental spectrum are due to the ^{12}CO isotopomer.

Rhodium(I) Hydrides and Carbonyl Hydrides. The protonation chemistry of triphenylphosphine complexes of Rh(I) hydrides and carbonyl hydrides differs from that of the Co(I) and Ir(I) congeners in that the putative cationic dihydride species formed initially loses dihydrogen rapidly and irreversibly. The reason(s) for this facile reductive elimination process and the anomalous reactivity of rhodium in the cobalt triad is not clear. However, the trend is in accord with the observations of Vaska and coworkers, who found that Rh(I) occupies a position intermediate between Co(I) and Ir(I) in its chemical reactivity, being less prone to undergo oxidative addition or, alternatively, that reductive elimination from Rh(III) is easier than for Co(III) or Ir(III) analogues.[15]

Reaction of **1** with a toluene suspension of $(Ph_3P)_3Rh(CO)H$ produces 1 equiv of hydrogen and $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$ (**7**) in 85% isolated yield; the $[N(SO_2CF_3)_2]^-$ and $[PhC(SO_2CF_3)_2]^-$ salts may be prepared in an analogous way from $HN(SO_2CF_3)_2$ and $PhCH(SO_2CF_3)_2$ and have quite similar properties.[16] In dichloromethane, **7** exhibits a single, strong Rh–CO stretching band at 2026 cm^{-1}. Its ^{31}P NMR spectrum is the A_2B portion of an A_2BX pattern indicative of the usual square-planar coordination geometry about Rh(I) with P_A and P_B cis and trans, respectively, to the carbonyl ligand (vide infra). The ^{13}C NMR spectrum of $[(Ph_3P)_3Rh(^{13}CO)][HC(SO_2CF_3)_2]$, prepared by exchange of **7** in CH_2Cl_2 with ^{13}CO, exhibits a doublet of doublets of triplets (J = 95, 66, and 16 Hz, respectively) centered at 186.8 ppm. The 161.9-MHz ^{31}P NMR spectrum of this ^{13}C-labeled derivative comprises overlapping A_2BMX and A_2BX spin multiplets (A, B = ^{31}P, M = ^{13}C, X = ^{103}Rh) in a 2:1 ratio because the carbonyl is only 65% ^{13}C labeled. The spectrum is second order because the coupling constants are greater than the chemical shift difference between the ^{31}P nuclei. It is a sensitive function of the relative signs of the coupling constants between M and X with the two different types of ^{31}P nuclei but not of the sign of J_{AB}. The simulated spectrum, (Figure 1; cf. Experimental Section) yields the parameters δ_{P_A} = 24.25, δ_{P_B} =

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(9) Siedle, A. R.; Gleason, W. B.; Newmark, R. A.; Pignolet, L. H. *Organometallics* **1986**, *5*, 1969.
(10) Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 767.
(11) Siedle, A. R.; Howells, R. D. U.S. Patent 4 556 720, 1985.
(12) Sacco, A.; Ugo, R. *J. Chem. Soc. A* **1964**, 3274.
(13) Gosser, L. W. *Inorg. Chem.* **1976**, *15*, 1348.
(14) Miller, J. S.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1067.
(15) Bird, P.; Harrod, J. F.; Than, K. A. *J. Am. Chem. Soc.* **1974**, *96*, 1222.
(16) Vaska, L.; Chen, L. S.; Miller, M. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671.

23.13, $J_{P_AP_B} = 27.9$ Hz, $J_{P_ARh} = -122.8$ Hz, $J_{P_BRh} = -129.4$ Hz, $J_{P_AC} = -17.5$ Hz, $J_{P_BC} = 95.6$ Hz, and $J_{RhC} = 66$ Hz. The absolute signs cannot be determined from the available data. However, one-bond J_{RhP} coupling constants are likely negative[17] and opposite signs for cis and trans J_{PC} have been reported for compounds of the type $(R_3P)Pt(C_2H_4)_2$ with the trans coupling being positive.[18]

Likewise, protonation of $(diphos)_2RhH$ (diphos is an abbreviation for $Ph_2PC_2H_4PPh_2$) and $[(PhO)_3P]_4RhH$ with **1** affords $[(diphos)_2Rh][HC(SO_2CF_3)_2]\cdot C_7H_8$ (**8**)[12] and $[\{(PhO)_3P\}_4Rh][HC(SO_2CF_3)_2]$ (**9**), respectively. The reactivity of the (triphenyl phosphite)rhodium hydride is striking in view of the inertness of the cobalt analogue (vide supra).

Protonation of $(Ph_3P)_4RhH$ with an equimolar amount of **1** or **2** is distinctive in that it results in loss of both hydrogen and 1 equiv of triphenylphosphine with formation in high yield of salts of the 14-electron Rh(I) cation $[(Ph_3P)_3Rh]^+$. Saltlike $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$ (**10**) and $[(Ph_3P)_3Rh][PhC(SO_2CF_3)_2]$ (**11**) are insoluble in aromatic hydrocarbons, and when the reactions are carried out in toluene, **10** and **11** separate as analytically pure, red [λ_{max} (CH_2Cl_2) for **10** 503 nm, log ϵ 2.73] microcrystals that, although their solutions are extremely reactive toward oxygen, may be exposed to air for at least 1 h without apparent change.[19,20] Use instead of fluorocarbon acids having longer perfluoroalkyl groups leads to materials having significantly greater hydrocarbon solubility. Thus, saturated solutions of $[(Ph_3P)_3Rh][HC(SO_2C_8F_{17})_2]$ (**12**) and $[(Ph_3P)_3Rh][HC(SO_2C_4F_9)_2]$ (**13**) in toluene are ca. 0.4 M. Qualitatively **12** and **13** are more reactive toward oxygen than **10** and turn brown on standing in air for ca. 1 h.

The S–O stretching frequencies in **10**–**13** occur at 1345 and 1100 cm^{-1}, compared with 1330 and 1085 cm^{-1} in the piperidinium salt of $[HC(SO_2CF_3)_2]^-$. These data, along with the observation of only one singlet at 81.56 ppm in the ^{19}F NMR spectrum of **10**, provide evidence that the fluorocarbon acid conjugate bases are not coordinated to the metal center through one or both sulfonyl oxygen atoms, for such a bonding mode would be expected to exert significant perturbation on ν_{SO} as well as the ^{19}F chemical shifts. Coordination of the fluorocarbon anions to rhodium through carbon is excluded on the basis of the undecoupled ^{13}C NMR spectrum of **12** in toluene, in which the $[HC(SO_2C_8F_{17})_2]^-$ methine carbon appears as a doublet at 61.2 ppm with $J_{CH} = 186$ Hz and with no evidence of spin coupling to ^{103}Rh. The C–H coupling constant is that expected for sp^2-hybridized carbon. Further, the conductance of a 1×10^{-3} M solution of **10** in dichloromethane is 56 Ω^{-1} cm^2 mol^{-1}, consistent with behavior as a 1:1 electrolyte.

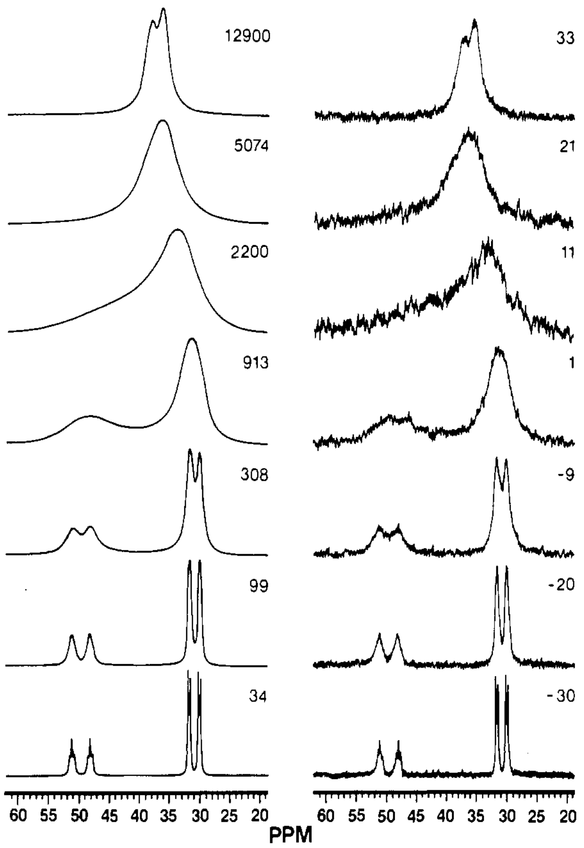
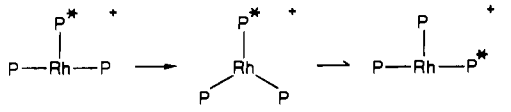


Figure 2. Calculated (left, τ^{-1} given in s^{-1}) and experimental (right, temperatures given in °C) $^{31}P\{^1H\}$ DNMR spectra of $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$.

Evidence for stereochemical nonrigidity of $[(Ph_3P)_3Rh]^+$ in **10** dissolved in dichloromethane is provided by ^{31}P DNMR spectroscopy. The ^{31}P NMR spectra obtained from −80 to −30 °C comprise the A_2B portion of an A_2BX pattern ($X = {}^{103}Rh$) with $\delta_A = 30.8$, $\delta_B = 49.4$, $J_{AX} = 134$ Hz, $J_{BX} = 244$ Hz, and $J_{AB} = 32$ Hz. As the temperature is increased, both resonances broaden and then coalesce to form an A_3X doublet, $\delta_A = 38.1$ ppm and $J_{AX} = 172$ Hz, in a manner typical of a dynamic equilibrium interconverting the two types of ^{31}P environments. Spin coupling between ^{103}Rh and ^{31}P is preserved in both low- and high-temperature regimes, indicating that the fluxional process is intramolecular. Lifetimes for triphenylphosphine exchange and free energies of activation were determined between −30 and +33 °C, and Figure 2 shows the observed and calculated DNMR spectra. A least-squares linear fit of ΔG^* with temperature gives $\Delta H^* = 13.8 \pm 0.9$ kcal/mol and $\Delta S^* = 5 \pm 4$ eu. These results are interpretable in terms of a ground-state T-shaped P_3Rh unit, similar to that found by X-ray crystallography in $[(Ph_3P)_3Rh][ClO_4]$,[19] in which permutation of triphenylphosphine ligands occurs through a Y-shaped C_{3v} transition state or intermediate as shown in eq 2. Molecular orbital calculations on isoelectronic $(CH_3)_3Au$ indicate that this species is orbitally degenerate and undergoes a Jahn–Teller distortion from C_{3v} symmetry toward a lower energy T-shaped conformation,[21] and a theoretical analysis of cation deformations in $[(Ph_3P)_3Rh][ClO_4]$ has also been performed.[22] We propose that a dynamic distortion obtains for $[(Ph_3P)_3Rh]^+$ and that the molecular orbital calculations of Hoffmann, Albright, and Kochi[21] for ML_3 fragments have general applicability. An alternative process, coordination of $[HC(SO_2CF_3)_2]^-$ to $[(Ph_3P)_3Rh]^+$ to form a fluxional, five-coordinate Rh intermediate, is discounted because addition of an equimolar amount of $[(n\text{-}C_3H_7)_4N][HC(SO_2CF_3)_2]$ produces no observable effect on the DNMR spectra. However, addition of Ph_3P does lead to broadened ^{31}P NMR signals and loss of ^{103}Rh–^{31}P spin coupling, which indicates that associative exchange with added ligand occurs. The ^{31}P NMR spectrum of the related compound $(Me_3P)_3RhBF_4$ at −25 °C is reported to be a doublet.[23] It is possible that the limiting low-temperature spectrum, not obtained for $[(Me_3P)_3Rh]^+$, would show this species also to be stereochemically nonrigid. Alternatively, a weak Rh–F interaction may occur in this compound. The low-temperature ^{31}P NMR spectrum of $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$, which may be viewed as that of an ion having a T-shaped P_3Rh ground-state geometry,



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[17] Hyde, E. M.; Kennedy, J. D.; Shaw, B. L.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1977**, 1571.

[18] Harrison, N. C.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1337.

[19] Yared, Y. W.; Miles, S. L.; Bau, R., Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7176. These workers also first prepared and structurally characterized $[(Ph_3P)_3Rh][ClO_4]$.

[20] Wilkinson, G. U.S. Patent 3794671, 1974. The conductance of $[(Ph_3P)_3Rh][BF_4]$ in CH_3NO_2 was considerably less than that expected for a 1:1 electrolyte, and coordination of $[BF_4]^-$ to Rh via a B–F–Rh bond was proposed.

[21] Komiya, S.; Albright, T. A.; Hoffman, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

[22] Dedieu, A.; Hyla-Kryspin, I. *J. Organomet. Chem.* **1981**, *220*, 115.

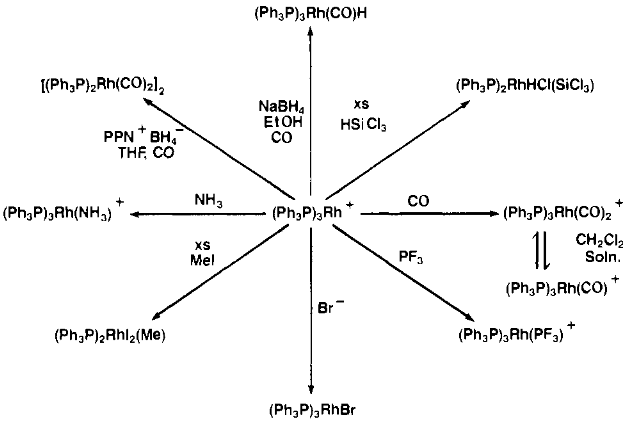
[23] Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 511.

Table I. Chemical Shifts and Coupling Constants in $[(Ph_3P_A)_2(Ph_3P_B)Rh(MX)][CH(SO_2CF_3)_2]$[a]

M	X	δ_{P_A}	δ_{P_B}	δ_M	δ_X	J_{AB}	J_{AM}	J_{BM}	J_{AX}	J_{BX}	J_{MX}	J_{RhP_A}	J_{RhP_B}	J_{RhM}	J_{RhX}
N	H_3	35.4	46.1	−24.2	1.2	40.2	1.9	28.1	2.9	2.9	67.7	142	169	10.2	
P	F_3	35.7	17.3	111.5	−19.0	42	60	492	7.4	44	1350	116	147	308	24.9
C	O	24.2	23.1	186.8		37.9	−17.5	95.6				−122.8	−129.4	66	

[a] *J* values are in hertz.

Scheme I



may be compared with data for a series of compounds of the type $PhP(C_3H_6PPh_2)_2RhX$. In the latter, it was found that J_{RhP} for the unique ^{31}P nucleus was scaled with the trans influence of the substituent X.[24] In $[(Ph_3P)_3Rh]^+$, this coupling is quite large, 244 Hz, and this value may be taken to represent the trans influence of no ligand at all.

Reactions of $[(Ph_3P)_3Rh]^+$. Carbonylation. In this work, most attention has focused on carbonylation reactions (cf. Scheme I). The literature surrounding this chemistry is confusing. Wilkinson reported that $[(Ph_3P)_3Rh(CO)][BF_4]$ was obtained from $(Ph_3P)_3RhFBF_3$, whose formula is written so as to emphasize the proposed coordination of $[BF_4]^-$ in this compound.[20] Reed and Bau obtained $[(Ph_3P)_3Rh(CO)_2][ClO_4]$ from $[(Ph_3P)_3Rh][ClO_4]$.[19] Reddy et al. reported that $[(Ph_3P)_3Rh(CO)_2][ClO_4]$ could be obtained in orange (ν_{CO} 2018 cm^{-1}) and yellow (ν_{CO} 2025 and 2012 cm^{-1}) forms depending on reaction conditions.[25] A further intimation of the equilibria involved in the $[(Ph_3P)_3Rh]^+$–CO system may also be found in earlier work by Schrock and Osborn, who prepared $[(Ph_3P)_3Rh(CO)_n]^+$ salts (n = 1, 2) from $[(C_8H_{12})Rh(PPh_3)_2]^+$, CO, and Ph_3P.[26]

Pure $[(Ph_3P)_3Rh(CO)_2][HC(SO_2CF_3)_2]$ (**14**) is readily obtained in quantitative yield by treatment of *solid* $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$ with carbon monoxide at atmospheric pressure. The reaction may be followed visually, as red **10** is transformed to yellow **14**. It might be thought that this solid–gas carbonylation reaction involves $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$ as an intermediate, but, insofar as this formula comprehends a solid having the same positional atomic relationships within and between unit cells as **7** as well as the same reactivity, such is not the case. Even under low partial pressure of CO, none of the carbonylrhodium species can be detected by infrared analysis. In fact, solid $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$ is completely unreactive toward CO under conditions in which formation of **14** occurs. A species recognizable as $[(Ph_3P)_3Rh(CO)]^+$ could probably be discerned within the reaction zone if it were viewed on a 10^{-9} M scale, but atomic organization on a larger scale could be quite different from that in **7**.

That **14** is in fact a rhodium dicarbonyl complex is established by NMR spectroscopy (vide infra) and chemical derivatization. Its reaction with neat $(PhO)_3P$ yields $[\{(PhO)_3P\}_4Rh][HC(SO_2CF_3)_2]$ as the sole rhodium-containing species detectable by ^{31}P NMR. The yield of coproduct, carbon monoxide, measured volumetrically, was 99% of the theoretical value. The infrared spectrum of **14** in dichloromethane demonstrates two Rh–CO stretching bands at 2019 (s) and 1988 (m) cm^{-1}, suggestive of a cis arrangement of the two carbonyl ligands.

NMR spectra of compounds containing the $[(Ph_3P)_3Rh(CO)_2]^+$ ion are complicated by dissociation of both Ph_3P and CO ligands, with the former process having the higher activation energy. The $^{31}P\{^1H\}$ NMR spectrum of $[(Ph_3P)_3Rh(CO)_2][HC(SO_2CF_3)_2]$ in CD_2Cl_2 at room temperature comprises a singlet, $w/2$ = 17 Hz, at 22.4 ppm. This, when the solution is cooled, is transformed into a 113-Hz doublet at −40 °C; the spectrum is then invariant down to the freezing point of the sample. Loss of ^{31}P–^{103}Rh spin coupling is indicative of triphenylphosphine dissociation. The ^{13}C NMR spectrum of $[(Ph_3P)_3Rh(^{13}CO)_2][HC(SO_2CF_3)_2]$, prepared from **10** and ^{13}CO, is a broad ($w/2$ = 50 Hz) singlet at 22 °C that is transformed on cooling to ≤−60 °C into a doublet of quartets centered at −198.6 ppm with J_{CRh} = 50 Hz and J_{CP} = 14 Hz. These quartets coalesce to a broad doublet at −108 °C, but because the solvent resonance remains sharp, this effect is not due primarily to viscosity broadening. Evidently the limiting low-temperature spectrum has not been obtained, and it is therefore not possible to ascertain the solution-phase ground-state structure of the $[(Ph_3P)_3Rh(CO)_2]^+$ ion. The NMR data are merely consistent with a trigonal-bipyramidal structure containing equatorial Ph_3P and apical CO ligands. The converse has been proposed for $[(Ph_3P)_2Rh(CO)_3]^+$.[27] However, five-coordinate complexes often have quite low barriers to intramolecular rearrangements and, in the absence of definitive low-temperature NMR data, alternative structures cannot be ruled out.

The lability of coordinated CO in solutions of $[(Ph_3P)_3Rh(CO)_2][HC(SO_2CF_3)_2]$ was discovered by James Hill in this laboratory. When nitrogen is bubbled through a solution of **14** in dichloromethane, $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$, identified by infrared and ^{31}P NMR analyses, is produced; the dicarbonyl complex is regenerated by passing carbon monoxide through the solution. The equilibrium shown in eq 3 ensures that recrystallization of **14** under other than a CO atmosphere leads to formation of the monocarbonyl compound. This equilibrium is, however, slow on the NMR time scale, for separate ^{13}C and ^{31}P resonances are observed for each species in a mixture of the two, and it thus does not account for the dynamic behavior of **14**.

$$(Ph_3P)_3Rh(CO)_2^+ \rightleftharpoons (Ph_3P)_3Rh(CO)^+ + CO \qquad (3)$$

Solid $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$ does not react with PF_3 at pressures of up to 50 psi. However, in dichloromethane solution, $[(Ph_3P)_3Rh(PF_3)][HC(SO_2CF_3)_2]$ (**15**) readily forms. The PF_3 ligand is evidently labile, but at −60 °C, first-order ^{19}F and ^{31}P spectra were observed. Chemical shifts and coupling constants for this A_2BMX_3Y spin system are given in Table I.

Other Reactions. The $[(Ph_3P)_3Rh]^+$ cation readily forms complexes with Lewis bases. Solid **10** readily absorbs ammonia at 700 mm pressure to produce $[(Ph_3P)_3Rh(NH_3)][HC(SO_2CF_3)_2]$ (**16**), whose ^{31}P NMR spectrum is a typical A_2BX pattern with δ_{P_A} 35.4, δ_{P_B} 46.1, J_{AX} = 142 Hz, J_{BX} = 169 Hz, and J_{AB} = 40 Hz. The ^{15}N analogue was prepared by using $^{15}NH_3$. Its ^1H NMR spectrum discloses a doublet of quartets centered at 1.15 ppm with $J_{^{15}NH}$ = 67.7 Hz; the two 2.8-Hz $^3J_{PH}$ coupling constants are fortuitously degenerate. The ^1H-decoupled ^{15}N spectrum is the M portion of an A_2BMX pattern and comprises

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[24] Christoph, G. G.; Blum, P.; Liu, W. C.; Elia, A.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 894.

[25] Reedy, G. K. N.; Ramesh, B. R. *J. Organomet. Chem.* **1974**, *67*, 443.

[26] Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. Figure 4 in this reference shows reversible addition of CO to $[(Ph_3P)_3Rh(CO)]^+$.

[27] Long, G. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979.

a 28-Hz doublet of 10.2-Hz doublets of 1.9-Hz triplets centered at −24.2 ppm from which J_{NRh} = 10.2 Hz, J_{NP_A} = 1.9 Hz, and J_{NP_B} = 1.9 Hz. Other NMR data are given in Table I. Compound **16** is an uncommon example of a Rh(I) ammine complex for which ^{15}N data are available.[28]

In dichloromethane, **10** reacts with nitric oxide to form $[(Ph_3P)_2Rh(NO)_2][HC(SO_2CF_3)_2]$ (identified by comparison of its infrared spectrum with that of the $[BF_4]^-$ salt[29]) and with lithium bromide in tetrahydrofuran to form $(Ph_3P)_3RhBr$. Reaction with excess trichlorosilane in dichloromethane solvent yields $(Ph_3P)_2RhHCl(SiCl_3)$,[30] and excess CH_3I provides $CH_3Rh(Ph_3P)_2I_2$ rather than the anticipated oxidative-addition product.[5] The compound $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$ catalyzes isomerization of 1-pentene to 2- and 3-pentenes and the cyclotrimerization of hexafluoro-2-butyne to hexakis(trifluoromethyl)benzene; no adducts between **10** and 1-pentene, hexafluorobutyne, diphenylacetylene, or 1,4-diphenylbutadiene were detectable by ^{31}P NMR, and so it appears that the concentrations of the intermediates in the catalytic processes are quite low. Propionaldehyde undergoes stoichiometric decarbonylation to form **7**.

The course of reduction of $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$ is sensitive to experimental conditions. Reduction by $NaBH_4$ in ethanol under CO yields $(Ph_3P)_3Rh(CO)H$, whereas that by $[PPN][BH_4]$ in tetrahydrofuran yields $[(Ph_3P)_2Rh(CO)_2]_2$ (PPN = bis(triphenylphosphine)nitrogen(1+)).

Advantage may be taken of the slow exchange of **10** with Ph_3P (vide supra). Although **10** is quite soluble in organic solvents, it may be used to attach the $[(Ph_3P)_2Rh]^+$ moiety to functionalized polymers, thereby providing Rh(I) in an insoluble form that may be readily retrieved from reaction mixtures. Thus, when triphenylphosphine-substituted polystyrene is stirred with **10** in dichloromethane, the surface of the pale orange resin becomes red, indicating that $[(Ph_3P)_2Rh]^+$ units have become bonded to the phosphine donor sites on the polymer.[11]

Oxidation of $[(Ph_3P)_2Rh(CO)_2]_2$. Treatment of $[(Ph_3P)_2Rh(CO)_2]_2$ with 2 equiv of $H_2C(SO_2CF_3)_2$ in toluene under a CO atmosphere produces [*trans*-$(Ph_3P)_2Rh(CO)_2][HC(SO_2CF_3)_2]$ (**17**), with ν_{CO} 2099 (s) and 2044 (m) cm^{-1} (CH_2Cl_2 solution). This is the first example of a reaction in which $H_2C(SO_2CF_3)_2$ unambiguously behaves as an oxidizing agent; because the ligands surrounding rhodium are all electrically neutral, a one-electron transfer must be involved in the formation of **17**. The $[(Ph_3P)_2Rh(CO)_2]^+$ cation has been reported to form upon reaction of $[(Ph_3P)_2Rh(NO)(CH_3CN)_2][PF_6]_2$ with CO at 10 atm pressure, but no characterization data are available.[31] Here, the composition and stereochemistry in **17** are defined by the A_2MX_2 NMR spectra (A = ^{13}C, M = ^{103}Rh, and X = ^{31}P) of the ^{13}C-labeled analogue, prepared by exchange of **17** with ^{13}CO. At ≤−60 °C, the ^{13}C NMR spectrum of **17** in CD_2Cl_2 reveals a doublet of triplets centered at 185.4 ppm with J_{CP} = 14.8 Hz and J_{CRh} = 66 Hz. The phosphorus NMR spectrum displays the same pattern with $\delta_{^{31}P}$ = 26.6 ppm and J_{PRh} = 106 Hz. As the temperature is increased, the ^{31}P resonance becomes a 106-Hz doublet. Concomitantly, the ^{13}C resonance becomes a broad singlet and ^{13}C–^{103}Rh coupling is lost. These data indicate that rapid intermolecular CO exchange occurs at ≥−60 °C. Also illustrative of lability of one of the coordinated CO ligands is the reaction of **17** with acetonitrile, which produces [*trans*-$(Ph_3P)_2Rh(CO)(CH_3CN)][HC(SO_2CF_3)_2]$ (**18**), with $\delta_{^{31}P}$ 30.8 and $\delta_{^1H}$ 1.43 (CH_3CN). The crystal structure of **18** has been determined by Dr. W. B. Gleason and will be reported elsewhere.

Use of Other Fluorocarbon Acids. Perfluoroalkanesulfonic acids, R_fSO_3H, where R is a long-chain perfluoroalkyl group such as C_8F_{17}, are also useful for synthesis of $[(Ph_3P)_3Rh]^+$ salts that have high hydrocarbon solubility. $C_8F_{17}SO_3H$ has a long hydrophobic tail; the crystalline solid does not absorb significant amounts of atmospheric moisture, and it may be conveniently handled in air. Qualitatively, it appears to exhibit the same reactivity with organometallic compounds as CF_3SO_3H.

Table II. Analytical Data

compd	results: calcd (found), %
$[(Ph_2PC_2H_4PPh_2)_2CoH_2]$-$[HC(SO_2CF_3)_2]$ (**3**)	C, 58.1 (58.3); H, 4.5 (4.3); F, 10.0 (10.4); S, 5.6 (5.8)
$[(Ph_2PC_2H_2PPh_2)_2CoH_2]$-$[HC(SO_2CF_3)_2]$ (**4**)	C, 58.3 (57.8); H, 4.5 (4.5); Co, 5.2 (4.8); F, 10.1 (10.3); P, 11.0 (11.3)
$[(Ph_2PC_2H_4PPh_2)_2IrH_2]$-$[HC(SO_2CF_3)_2]$ (**5**)	C, 52.4 (52.6); H, 4.1 (4.0)
$[(Ph_3P)_3Ir(CO)H_2]$-$[HC(SO_2CF_3)_2]$ (**6**)	C, 54.1 (54.1); H, 3.7 (4.0); F, 8.9 (8.6); S, 5.0 (4.8)
$[(Ph_3P)_3Rh(CO)]$-$[HC(SO_2CF_3)_2]$ (**7**)	C, 58.2 (57.7); H, 3.8 (3.8); P, 7.8 (7.8); Rh, 8.6 (8.5); S, 5.4 (5.9)
$[(Ph_2PC_2H_4PPh_2)_2Rh]$-$[HC(SO_2CF_3)_2]\cdot C_7H_8$ (**8**)	C, 58.6 (58.1); H, 4.5 (4.5)
$[\{(PhO)_3P\}_4Rh][HC(SO_2CF_3)_2]$ (**9**)	C, 55.5 (55.2); H, 3.8 (3.9)
$[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$ (**10**)	C, 58.6 (58.3); H, 3.9 (4.0); F, 9.9 (10.0); P, 8.0 (8.0); Rh, 8.8 (8.7); S, 5.5 (5.2)
$[(Ph_3P)_3Rh][PhC(SO_2CF_3)_2]$ (**11**)	C, 60.8 (60.5); H, 4.0 (4.0)
$[(Ph_3P)_3Rh][HC(SO_2C_8F_{17})_2]$ (**12**)	C, 45.6 (45.9); H, 2.5 (2.4); F, 34.6 (34.0); Rh, 5.5 (5.1)
$[(Ph_3P)_3Rh][HC(SO_2C_4F_9)_2]$ (**13**)	C, 51.5 (50.9); H, 3.1 (3.2); F, 23.3 (23.7); Rh, 7.0 (7.1)
$[(Ph_3P)_3Rh(CO)_2]$-$[HC(SO_2CF_3)_2]$ (**14**)	C, 57.8 (57.2); H, 3.8 (3.6); F, 9.3 (9.1); P, 7.6 (7.7); Rh, 8.4 (8.2); S, 5.2 (5.2)
$[(Ph_3P)_3Rh(PF_3)]$-$[HC(SO_2CF_3)_2]$ (**15**)	C, 54.5 (54.9); H, 3.7 (3.5)
$[(Ph_3P)_3Rh(NH_3)]$-$[HC(SO_2CF_3)_2]$ (**16**)	C, 57.7 (57.8); H, 4.1 (4.3); N, 1.2 (1.1)
$[(Ph_3P)_2Rh(CO)_2]$-$[HC(SO_2CF_3)_2]$ (**17**)	C, 51.1 (51.0); H, 3.2 (3.2); P, 6.4 (6.2); Rh, 10.7 (10.8)

Experimental Section

Reactions were carried out, unless otherwise specified, under an oxygen- and water-free atmosphere. Toluene and hexane were distilled from Na–K alloy and CH_2Cl_2 from CaH_2. CD_2Cl_2 used as an NMR solvent was stored over CaH_2, and NMR samples of air-sensitive materials were prepared on a vacuum line. NMR spectra were obtained with Varian XL-200 and XL-400 instruments at 200 and 400 MHz, respectively (^1H), on CD_2Cl_2 solutions. Positive chemical shifts are downfield relative to internal $(CH_3)_4Si$ or $CFCl_3$ and external 85% H_3PO_4 or saturated aqueous NH_4NO_3. Analytical data for new compounds reported are gathered in Table II. The fluorocarbon acids prepared by the method of Koshar and Mitsch[32] were provided by Robert Koshar, 3M Industrial and Consumer Sector Research Laboratory.

Dynamic NMR spectra were calculated on a DEC VAX 11/580 computer with use of DYNAMAR, a program written for intramolecular exchange by Meakin[33] that has been modified by S. T. McKenna at the University of California at Berkeley. The program was further modified by us to include routines to automatically vary the exchange rate to fit either a line width or a valley between two peaks. Temperatures were calibrated by using a neat methanol sample.[34] ^{31}P NMR spectra were obtained with a 2-kHz sweep width and a 0.5-s acquisition time. A total of 100 transients were accumulated at each temperature with a 1.1-s recycle time. Low-power Waltz-modulated ^1H decoupling, centered at 0 ppm, was used to minimize rf heating of the sample.

Analysis of the ^{31}P NMR spectrum of **7** began with the outside multiplets, which are almost first order. Their frequencies were used to estimate the absolute values of the coupling constants. Spectra were then calculated for the four possible combinations of signs. Coupling constants and chemical shifts were then adjusted by using an iterative computer program to minimize the root mean square (rms) error between observed and calculated positions of the six absorptions at each end of the spectrum. The calculated spectrum in Figure 1 shows a rms deviation of <0.3 Hz from the observed spectrum. Spectra calculated for other possible sign combinations show good fits for the outer multiplets but differences of several hertz in the calculated frequencies of the peaks near the center

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(28) Mason, J. *Chem. Rev.* **1981**, *81*, 205.
(29) Dolcetti, G.; Hoffman, N. W.; Collman, J. P. *Inorg. Chim. Acta* **1972**, *6*, 531.
(30) de Charentenay, F.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 787.
(31) Connelley, N. G.; Green, M.; Kuc, T. A. *J. Chem. Soc., Chem. Commun.* **1974**, 542.
(32) Koshar, R. J.; Mitsch, R. A. *J. Org. Chem.* **1973**, *38*, 3358.
(33) Meakin, P.; Muetterties, E. L.; Tebbe, F. N.; Jesson, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 4701.
(34) Siedle, A. R.; Newmark, R. A.; Kruger, A. A.; Pignolet, L. H. *Inorg. Chem.* **1981**, *20*, 3399.

of the spectrum, where second-order effects are greatest. The calculated spectrum for the ^{12}C isotopomer fits the observed spectrum with a rms frequency error of <0.2 Hz. The $^{13}C/^{12}C$ isotope effect on ^{31}P shifts is <0.01 ppm.

Protonation of $(diphos)_2CoH$. Toluene, 15 mL, was added to 0.42 g of $(diphos)_2CoH$[35] and 0.14 g of $H_2C(SO_2CF_3)_2$ (0.5 mmol each). The red cobalt hydride dissolved and was decolorized as the yellow insoluble product formed. After the mixture was stirred for 12 h, $[(diphos)_2CoH_2][HC(SO_2CF_3)_2]$ (**3**) was collected on a frit, washed with toluene, and vacuum-dried. The yield was 0.51 g. Protonations of $(Ph_2PCH{=}CHPPh_2)_2CoH$,[35] $(diphos)_2IrH$,[36] $(Ph_3P)_3Ir(CO)H$ (Strem), $(Ph_3P)_3Rh(CO)H$ (Strem), $(diphos)_2RhH$,[12] and $[(PhO)_3P]_4RhH$[37] were carried out in a similar way to yield **4**–**9**, respectively.

Synthesis of $[(Ph_3P)_3Rh(^{13}CO)][HC(SO_2CF_3)_2]$. A solution of 3.3 g of 7 in 12 mL of CH_2Cl_2 was stirred for 16 h under a 430-mm pressure of 99 atom % ^{13}CO. Toluene, 5 mL, was added and the solution concentrated by bubbling nitrogen through the solution to provide the crystalline product. The crystallization procedure was repeated twice again to ensure removal of the dicarbonyl complex. Infrared analysis indicated that ca. 70% of the carbonyl groups contained ^{13}C: ν_{CO} 1978 cm^{-1}.

Synthesis of $[(Ph_3P)_3Rh][HC(SO_2CF_3)_2]$ (10). A solution of 2.8 g (10 mmol) of $H_2C(SO_2CF_3)_2$ in 15 mL of toluene was added with vigorous stirring to a slurry of 10.9 g (10 mmol) of $(Ph_3P)_4RhH$[38] in 90 mL of toluene. Hydrogen evolved. After it was stirred for 6 h, the reaction mixture was filtered in a drybox and the solid red product washed with fresh solvent and then vacuum-dried. The yield was 10.5 g (95%). This compound can be recrystallized by slow evaporation of a solution in CH_2Cl_2–PhMe. The $[N(SO_2CF_3)_2]^-$ and $[PhC(SO_2CF_3)_2]^-$ salts were prepared in the same way by using $HN(SO_2CF_3)_2$ or $PhCH(SO_2CF_3)_2$.

Synthesis of $[(Ph_3P)_3Rh][HC(SO_2C_8F_{17})_2]$. A mixture of 1.02 g of $(Ph_3P)_4RhH$ and 0.85 g of $H_2C(SO_2C_8F_{17})_2$ in 10 mL of CH_2Cl_2 was stirred for 3 h. The product was precipitated by addition of hexane and reprecipitated from CH_2Cl_2–hexane. The yield of red powdery **12** was 1.8 g. ^{19}F NMR (CH_2Cl_2): δ 113.95 (F1, adjacent to SO_2), 119.95 (F2), 121.76 (F3–5), 122.72 (F6), 126.17 (F7), 81.7 (F8).

A similar reaction between 0.92 g of $(Ph_3P)_4RhH$ and 0.46 g of $H_2C(SO_2C_4F_9)_2$ in toluene produced 0.65 g of **13**, which was precipitated with hexane three times. ^{19}F NMR (CH_2Cl_2): δ 114.17 (F1, adjacent to SO_2), 121.03 (F2), 126.08 (F3), 81.09 (F4).

Synthesis of $[(Ph_3P)_3Rh(CO)_2][HC(SO_2CF_3)_2]$. A 4.8-g quantity of **10** contained in a glass flask was attached to a vacuum line. The container was evacuated and backfilled to a pressure of 760 mm with CO. The red color of the starting material was discharged over the course of 4 h as bright yellow **14** formed. The yield was quantitative by ^{31}P NMR analysis. A similar reaction on one-tenth of this scale with ^{13}CO instead was used to prepare the ^{13}CO analogue.

A similar reaction with ammonia produced a quantitative yield of $[(Ph_3P)_3Rh(NH_3)][HC(SO_2CF_3)_2]$ (**16**), with ν_{NH} (Nujol) 3355, 3325, 3255 cm^{-1}.

Synthesis of $[(Ph_3P)_3Rh(PF_3)][HC(SO_2CF_3)_2]$. A 300-mL glass flask containing a solution of 1.0 g of **10** in 10 mL of CH_2Cl_2 was cooled in liquid nitrogen, evacuated, backfilled to 500 mm with PF_3, and then isolated from the vacuum line. As the solid reaction mixture began to melt, its color turned from red to yellow. After the mixture was warmed to room temperature, volatiles were removed under vacuum to provide 1.0 g of yellow **15**.

Synthesis of [*trans*-$(Ph_3P)_2Rh(CO)_2][HC(SO_2CF_3)_2]$. A solution of 0.24 g (0.33 mmol) of $[(Ph_3P)_2Rh(CO)_2]_2$[39] and 0.19 g (0.66 mmol) of $H_2C(SO_2CF_3)_2$ in 5 mL of toluene was stirred under 20 psi of CO. After 3 h, bright yellow **17** was collected on a Schlenk filter, washed with toluene, and vacuum-dried. The yield was 0.32 g. To prepare the ^{13}C-labeled derivative (ν_{CO} (CH_2Cl_2) 1997, 1935 cm^{-1}), 0.1 g of **17** in 2 mL of CH_2Cl_2 was stirred for 20 h under a 600-mm pressure of ^{13}CO, after which infrared analysis indicated that the exchange was >95% complete.

. Dissolution of **17** in CH_3CN followed by evaporation of this solvent produces a quantitative yield of $[(Ph_3P)_2Rh(CO)(CH_3CN)][HC(SO_2CF_3)_2]$ (**18**; ν_{CO} 2016 (s) cm^{-1}) by infrared analysis.

Polymer-Supported $[(Ph_3P)_2Rh]^+$. Triphenylphosphine-substituted polystyrene (Aldrich, 0.33 g) was stirred with a solution of 0.55 g of **10** in 6 mL of CH_2Cl_2. After 2.5 h, the resin, which had turned red, was isolated by filtration, washed with fresh solvent, and vacuum-dried. It contained 5.3% Rh. Its infrared spectrum contained characteristic absorptions of $[HC(SO_2CF_3)_2]^-$.

Cyclotrimerization of Hexafluoro-2-butyne. A 0.25-g sample of **10** was loaded into a Schlenk tube, and 7 mL of CH_2Cl_2 and 0.5 mL of hexafluorobutyne (liquid) were added by vacuum transfer. After the mixture was heated at 80 °C overnight, 0.1 g of $(CF_3)_6C_6$, identified by infrared and mass spectroscopy, separated.

Isomerization of 1-Pentene. A mixture of 0.05 g of **10**, 0.2 mL of 1-pentene, and 0.5 mL of CD_2Cl_2 was sealed in a 5-mm NMR tube. Analysis by ^{13}C NMR after 4 weeks revealed that the sample then contained *trans*-2-pentene and *cis*-2-pentene in a 9:1 ratio; no 1-pentene remained.

Hydroformylation of 1-Hexene. A 100-mL portion of toluene, 5 mL of 1-hexene, and 0.1 g of **14** were heated for 20 h under a 1000 psi pressure of 1:1 H_2–CO. GC analysis of the reaction mixture showed that heptaldehyde was produced in 73% yield.

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Registry No. **1**, 428-76-2; **2**, 40906-82-9; **3**, 114634-77-4; **4**, 114634-79-6; **5**, 88825-74-5; **6**, 114634-80-9; **7**, 98837-97-9; **8**, 114634-81-0; **9**, 114634-82-1; **10**, 88825-75-6; **11**, 98838-00-7; **12**, 88825-76-7; **13**, 98838-01-8; **14**, 98837-96-8; **15**, 114634-84-3; **16**, 114634-86-5; **17**, 114634-87-6; **18**, 114634-88-7; $(Ph_2PCH{=}CHPPh_2)_2CoH$, 70252-14-1; $(diphos)_2IrH$, 29189-86-4; $(diphos)_2RhH$, 29189-87-5; $[(PhO)_3P]_4RhH$, 24651-65-8; $[(Ph_3P)_2Rh(CO)_2]_2$, 20936-09-8; $(diphos)_2CoH$, 18433-72-2; $[(Ph_3P)_2Rh(NO)_2][HC(SO_2CF_3)_2]$, 114634-89-8; $(Ph_3P)_2RhHCl(SiCl_3)$, 18745-54-5; $CH_3Rh(Ph_3P)_2I_2$, 47829-28-7; $HN(SO_2CF_3)_2$, 82113-65-3; $(Ph_3P)_3Ir(CO)H$, 33541-67-2; $(Ph_3P)_3Rh(CO)H$, 17185-29-4; $(Ph_3P)_4RhH$, 18284-36-1; Ph_3P, 603-35-0; $F_3CC{\equiv}CCF_3$, 692-50-2; $(Ph_3P)_3RhBr$, 14973-89-8; $H_2C(SO_2C_8F_{17})_2$, 29214-34-4; $H_2C(SO_2C_4F_9)_2$, 29214-37-7; 1-pentene, 109-67-1; 1-hexene, 592-41-6; propionaldehyde, 123-38-6.

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(35) Bianco, V. D.; Doronzo, S.; Gallo, N. *Inorg. Synth.* **1980**, *20*, 206.

(36) Schunn, R. A. *Inorg. Chem.* **1970**, *9*, 2567.

(37) Levison, J. J.; Robinson, S. D. *Inorg. Synth.* **1972**, *13*, 109.

(38) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 58.

(39) Booth, B. L.; Casey, S.; Haszeldine, R. N. *J. Organomet. Chem.* **1982**, *226*, 289.