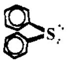
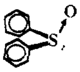
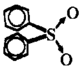
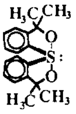
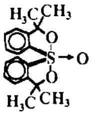
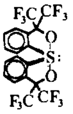
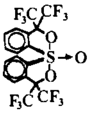
Table I. XPS Binding Energies of Sulfur Derivatives

compound	number	$S(2p_{3/2})$ binding energy (±0.1 eV)
	**1**[a]	163.4
	**2**[a]	166.0
	**3**[a]	167.8
	**4**[b]	165.8
	**5**[b]	167.6
	**6**[c]	166.5
	**7**[c]	168.4

[a] Purchased from Aldrich Chemical Company. [b] Reference 11c. [c] Reference 11d.

decrease electron density at the central atom. We find the XPS binding energies for stable 3c-4e bonded sulfur derivatives[11] (TBP and ψ-TBP geometries) give close correlations with the atomic populations calculated by Schwenzer and Schaefer[7] for analogous sulfur species. A similar correlation is observed for the diphenyl sulfane-sulfoxide-sulfone series. Table I lists the XPS binding energies for these sulfur derivatives.[12] Figure 1 shows plots of binding energies of related species vs the calculated[7] total atomic electron populations. The correlation coefficients for Figure 1a-c were 1.000, 0.999, and 1.000, respectively.

The linear correlation of the S(II) sulfane, the S(IV) sulfoxide, and the S(VI) sulfone (**1**, **2**, and **3**) (Figure 1a) is almost identical with that of the S(II) sulfane, the S(IV) 10-S-4 sulfurane, and the S(VI) 10-S-5 sulfurane oxide (**1**, **4**, and **5**) (Figure 1b) when the apical oxygen ligands are α,α-dimethylalkoxides. Both sulfoxides and sulfones are therefore thought to have small d-orbital occupancy comparable to that calculated[7] for the SH_4 and the SH_6 species and experimentally determined for **4** and **5** by their close correlation of XPS with the calculated[7] electron densities for SH_4 and SH_6. Analogues **6** and **7** with the more electronegative apical oxygens of α,α-bis(trifluoromethyl)alkoxy groups are also well correlated, together with **1**, to the calculated[7] electron densities of SH_2, SH_4, and SH_6 (Figure 1c). The electron withdrawal of the four CF_3 groups provides a binding energy increase of 0.6-0.8 eV relative to the four CH_3 groups of **4** and **5**.

Our results and interpretations contrast the papers of earlier investigators,[13] who suggested that the XPS binding energies of various sulfur derivatives, including **1**, **2**, and **3**, correlated with the "formal" oxidation states of the sulfur atom and, as a result, suggested that these data were inconsistent with the formation of polar bonds. Correlation of the XPS data of Table I with the calculated[7] atomic populations of SH_2, SH_4, and SH_6 suggests that d-orbital occupancy is low for all of these species.

In summary, the XPS data of Table I provides extensive insights into the nature of the bonding in sulfur species.

Acknowledgment. We thank the National Science Foundation for grants to P.G.G. and J.C.M., which supported this investigation. We also thank Dr. T. Hanks for determining the XPS binding energy of **1**.

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[11] For detailed discussions of the synthesis and properties of these sulfur derivatives, see: (a) Martin, J. C.; Perozzi, E. P. *Science* **1976**, *191*, 154. (b) Martin, J. C. *Science* **1983**, *221*, 509. (c) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001. (d) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6735.

[12] XPS analyses were carried out with Physics Electronics, Inc., ESCA-Auger-SIMS Model 555 or 548 spectrometers with Model 15-770 Specimen Introduction/Reaction Chambers. Samples were run on a polyethylene or polystyrene backing, which permitted an internal calibration against the C(1s) binding energy of the polymer (284.6 eV). All reported XPS binding energy values are ±0.1 eV.

[13] Lindberg, B. J.; Hamrin, D.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *1*, 286. Theodorakopoulus, G.; Csizmadia, I. G.; Robb, M. A.; Kucsman, A.; Kaopvits, I. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 293.

A Stable η^2-H_2 Complex of Cobalt. Role of the H-H Interaction in Hydrogen Transfer from Metal to Alkene

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Molecular hydrogen complexes of transition metals are much more widespread[1] than could be expected after the Kubas' seminal discovery of dihapto coordination of H_2 in $[M(CO)_3(PR_3)_2(H_2)]$ [M = Mo, W; R = Cy, *i*-Pr].[2] In actuality, the importance of nondisruptive activation of H_2 in hydrogenation reactions must be seriously reconsidered, particularly for group VIII elements since it is these which generally give rise to the most active catalyst systems. It is with η^2-dihydrogen and *cis*-dihydrides complexes of these metals and with their reactions with dimethyl maleate that the present communication is concerned.

The 16-electron fragments $[(PP_3)Rh]^+$ and $[(PP_3)Ir]^+$ [$PP_3 = P(CH_2CH_2PPh_2)_3$] add H_2 to give octahedral (OCT) *cis*-dihydrides of formula $[(PP_3)M(H)_2]^+$ (M = Rh,[3] **1**; Ir,[4] **2**). However, while the iridium compound maintains the classical dihydride structure both in the solid state and in solution regardless of the temperature, the rhodium complex converts into the trigonal-bipyramidal (TBP) η^2-H_2 isomer in solution above 173 K. The T_1(min) relaxation time of 120 ms and the JHD coupling constant of 18 Hz measured for the isotopomer $[(PP_3)Rh(HD)]^+$ are strongly diagnostic for a quite long H-H bond distance.[5] We have now synthesized the cobalt derivative $[(PP_3)Co(H_2)]PF_6$[6] (**3**) as dark red crystals by protonation of the TBP monohydride $[(PP_3)CoH]$[7] (**4**) in THF with $HOSO_2CF_3$ under argon atmo-

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[1] Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

[2] Kubas, G. C.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

[3] Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548.

[4] Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1987**, *326*, C79.

[5] (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (b) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1126.

[6] Compound **3** is stable for days in the solid state and in ambient temperature solutions under an argon atmosphere. Λ_M(nitroethane) = 86 Ω^{-1} cm^2 mol^{-1}. The IR spectrum contains no ν(Co-H). Anal. Calcd for $C_{42}H_{44}CoP_5F_6$: C, 57.55; H, 5.06; Co, 6.72; P, 17.67. Found: C, 57.63; H, 5.09; Co, 6.66; P, 17.45.

[7] Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1790.

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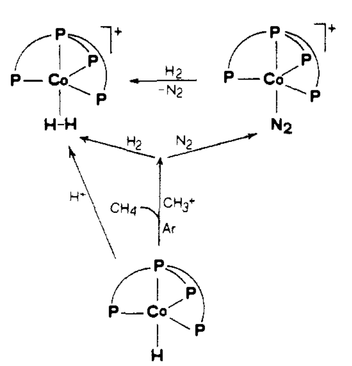
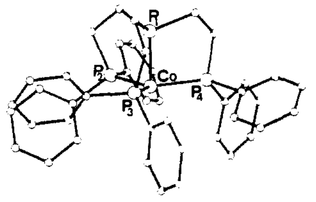
Scheme I



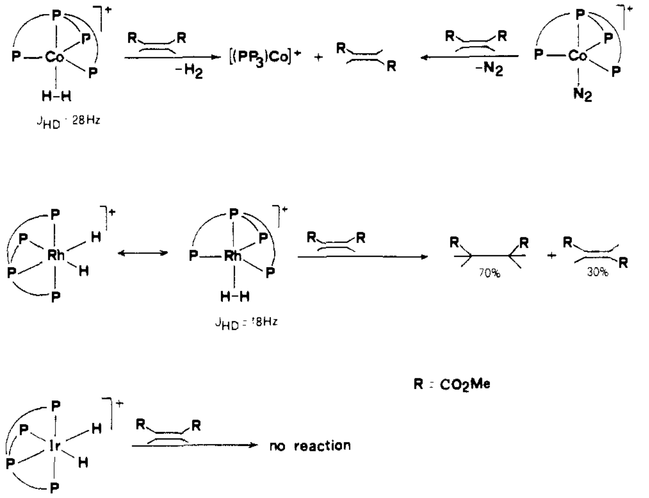
sphere, followed by $(NH_4)PF_6$ addition. Alternatively, 3 is prepared either by stirring the dinitrogen complex $[(PP_3)Co(N_2)]PF_6$[8] (5) under 1 atm of H_2 for 30 min or by addition of H_2 to the 16-electron system $[(PP_3)Co]^+$ generated in situ via reaction of 4 with $MeOSO_2CF_3$ (Scheme I). The $^{31}P\{^1H\}$ NMR spectrum of 3 (121.42 MHz, THF, H_3PO_4 reference) does not change over the temperature range 170–310 K and, in addition to the high-field septulet of PF_6^-, exhibits two singlets at 166.95 and 82.90 ppm (1:3). The two low field resonances are broadened by the cobalt quadrupole moment and sharpen but do not resolve into fine structure even at the lowest temperature. The position and relative intensity of the signals fall in the proper range of Co(I) TBP complexes with the PP_3 ligand.[9] In keeping with the spectroscopic results, an X-ray study of 3 proved that the $(PP_3)Co$ fragment has the shape of a trigonal-pyramid (I).[10]



I

Although not detected by the X-ray analysis, the presence of a dihydrogen molecule in the fifth position of the trigonal-bipyramid is clearly shown by the ^1H NMR spectrum of 3 (300 MHz, THF-d_8, Me_4Si reference). This exhibits a well-resolved multiplet (quartet of doublets, 2 H) at δ −10.92, the multiplicity of which arises from coupling of H_2 to the three equatorial phosphorus nuclei (JHP_{cis} = 30.7 Hz) and to the bridgehead phosphorus (JHP_{trans} = 27.2 Hz). On lowering the temperature, the resonance begins to broaden. At 170 K the multiplicity disappears ($w_{1/2}$ = 88 Hz), most likely as result of rapid relaxation rather than hindered H_2 rotation. Diagnostic features for Co-η^2-H_2 coordination in which the H–H bonding interaction is a strong one[5] are the following: the T_1 value (300 MHz, THF-d_8) is temperature-dependent and assumes a minimum value of 19 ms at 203 K [notice that the T_1 value of the monohydride 4 (300 MHz, 203 K, THF-d_8) is 110 ms]; a high value of JHD (27.8 Hz) is measured for the isotopomer $[(PP_3)Co(HD)]^+$.[11]

Scheme II



While it is reasonably expected that down the Co, Rh, and Ir triad, the oxidative addition prevails over the simple addition of H_2,[1,5b,12] it is certainly more intriguing that the rhodium complex alone is able to transfer hydrogen atoms to an alkene such as dimethyl maleate (DMMA). By stirring DMMA (1 mmol) under argon atmosphere with 1 (1 mmol) in THF at room temperature for 3 h, hydrogenation of the C–C double bond is predominantly carried out (Scheme II).[13] In contrast, the cobalt derivative in THF quantitatively isomerizes the olefin to dimethyl fumarate (DMFU). When an excess of DMMA is used, the reaction is catalytic with a turnover rate at 25 °C of 7 mol of DMFU per mol of metal per hour. In the isomerization process the H_2 ligand is displaced by the *cis*-olefin as shown by H_2 evolution, determined by GC. Moreover, the isomerization of DMMA to DMFU occurs under identical conditions also using the dinitrogen complex **5** (Scheme II). Finally, the iridium compound does not react with DMMA. A straightforward interpretation of these reactions is that which indicates the extent of the H–H bonding interaction as the governing factor for H_2 transfer from metal to alkene. In particular, for a strong H–H bond as in 3 (cobalt case: an example of totally arrested oxidative addition), dihydrogen behaves as a labile ligand which can be displaced by a competing substrate (an olefin). When the extent of the M → $H_2(\sigma^*)$ back-donation becomes of importance[1] (rhodium case), then an effective activation of H_2 is carried out by the metal, and the chemical combination of H_2 and olefin is feasible under very mild conditions. Finally, when the metal fragment oxidatively adds H_2 to give a classical dihydride (iridium case), the metal to hydrogen bonds are too strong to permit olefin insertion in the absence of a free coordination site at the metal.

Supplementary Material Available: ^1H NMR spectra of $[(PP_3)Co(H_2)]PF_6$ and $[(PP_3)Co(HD)](CF_3CO_2)]$ in the hydride region (2 pages). Ordering information is given on any current masthead page.

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(8) Compound **5** was prepared as red crystals by reacting the monohydride **4** in THF with $MeOSO_2CF_3$ under a nitrogen atmosphere (the evolution of CH_4 was determined by GC): IR $\nu(N{\equiv}N)$ = 2125 cm^{-1}; Λ_M(nitroethane) = 84 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6, 293 K) AM_3 spin system, δA = 161.35, δM = 65.25 ppm (JAM = 35.0 Hz). Anal. Calcd for $C_{42}H_{42}N_2CoP_5F_6$: C, 55.89; H, 4.69; N, 3.10; Co, 6.53; P, 17.16. Found: C, 55.64; H, 4.58; N, 3.14; Co, 6.42; P, 17.26.

(9) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616.

(10) Crystal data: $C_{42}H_{44}CoP_5F_6$; monoclinic, C_c, a = 16.876 (5) Å, b = 12.905 (2) Å, c = 18.896 (5) Å, β = 90°; Z = 4; D_{calcd} = 1.414 g cm^{-3}. At the present moment the structure is satisfactorily refined to an R value of 0.075 for 1712 observed reflections up to 2θ = 40°. Selected bond angles: P_1–Co–P_2 = 86.4 (7)°, P_1–Co–P_3 = 85.7 (7)°, P_1–Co–P_4 = 86.4 (7)°, P_2–Co–P_3 = 121.8 (7)°, P_2–Co–P_4 = 121.3 (7)°, P_3–Co–P_4 = 115.5 (7)°.

(11) The isotopomer $[(PP_3)Co(HD)](CF_3CO_2)$ was prepared by protonation of **4** in THF-d_8 with CF_3CO_2D. The compound can be precipitated by addition of C_2H_5OD.

(12) Bautista, M. Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780.

(13) Under 1 atm of H_2 in THF, the hydrogenation of DMMA is catalytic with turnover rates of 1.5 and 3 mol of dimethyl succinate per mol of metal per hour at 25 and 65 °C, respectively. After the consumption of the olefin, **1** is almost quantitatively recovered. In contrast, the $[(PP_3)Rh]^+$ system is not able to form an isolable complex with DMMA or DMFU, most likely because of steric crowding as the monosubstituted olefin $H_2C{=}CH(CO_2Me)$ does form an η^2-olefin complex. Mechanistically, the hydrogenation of DMMA by **1** may occur by initial proton transfer from the coordinated H_2 ligand to the olefin, followed by hydride addition. Reversal of the protonation step could be responsible for the observed isomerization. In this respect, it is worth noticing the **1** can be deprotonated by strong bases such as MeLi or KOBu^t to give the monohydride $[(PP_3)RhH]$.[3]