complexes and has pointed out that the latter is a very sensitive function of bond angle. In the above-mentioned Fe_2 compounds, a variation of bond angle of only ~6° gave a chemical shift variation of 80 ppm.[13c] We have structurally characterized several $(CO)_4W(\mu\text{-}PPh_2)_2ML_n$ complexes[10,11,15,16] and have tried to correlate structural results to ^{31}P NMR chemical shift data for these compounds. However, no obvious correlation exists among the metal–metal distances, M–P–M angles, and ^{31}P NMR data, as illustrated in Table V. This result is perhaps not too surprising since the metal–ligand combinations employed in the metal fragment linked to the $(CO)_4W(\mu\text{-}PPh_2)_2$ unit vary considerably. However, these data do point out serious problems in employing the μ-PR_2 chemical shift/metal–metal bond correlation.[14] The correlation appears to be best used for closely related series of compounds in which one or more members have been structurally characterized.

Stability and Reactivity of Complexes 1–4. Complexes **1–3** are stable in air for ~1 week in the solid state before showing signs of decomposition. However, solutions of the complexes decompose within minutes following air exposure. Complex **4**, although never obtained pure, is more air sensitive than **1–3**. The reactivities of complexes **1** and **2** were briefly explored with $Li[BHEt_3]$, CH_3Li, BuLi, and PhLi in attempts to form formyl and acyl derivatives in which these ligands could perhaps be stabilized by bridging between the metals, presumably with oxygen bound to the oxophilic Zr center. However, in no case were stable products isolated. Infrared monitoring showed that no reaction occurred when **1** and **2** were allowed to react with $Li[BHEt_3]$ and CH_3Li. Reaction of these complexes with PhLi at −78 °C did yield new ν_{CO} bands at lower energy (e.g., **1** + PhLi → bands at 1925, 1850, 1840 cm^{-1}) but all workup attempts led to decomposition of the product(s) formed. Also, infrared monitoring revealed that no reaction occurred when complexes **1** and **2** were heated (70 °C) or irradiated (>300 nm) in the presence of PhC≡CPh, $PMePh_2$, and CS_2.

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Registry No. **1**, 95465-26-2; **1**·$C_6H_{14}O_3$, 95465-28-4; **2a**, 95465-29-5; **2b**, 95465-30-8; **3**, 95465-31-9; **4**, 95465-32-0; $Fe(CO)_3(PPh_2H)_2$, 18399-67-2; $Fe(CO)_3(PCy_2H)_2$, 95483-60-6; *cis*-$W(CO)_4(PPh_2H)_2$, 70505-43-0; Cp_2ZrCl_2, 1291-32-3; Cp_2TiCl_2, 1282-40-2; $Li_2[Fe(CO)_3(PPh_2)_2]$, 95465-33-1; $Li_2[Fe(CO)_3(PCy_2)_2]$, 95465-34-2; $Li_2[W(CO)_4(PPh_2)_2]$, 88930-39-6; $Fe(CO)_5$, 13463-40-6; PPh_2H, 829-85-6; PCy_2H, 829-84-5.

Supplementary Material Available: Table of anisotropic thermal parameters, structure factors, and bond lengths and angles for **1** (22 pages). Ordering information is given on any current masthead page.

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(17) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise group 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Synthesis and Molecular Structures of Diorganophosphido-Bridged Heterobimetallic Complexes

R. T. BAKER,* T. H. TULIP, and S. S. WREFORD

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The "metal-containing bis(phosphine)" $Cp_2Hf(PEt_2)_2$ reacts with $Ni(CO)_4$, $Fe_2(CO)_9$, and $(NBD)Mo(CO)_4$ to form the diethylphosphido-bridged heterobimetallic complexes $Cp_2Hf(\mu\text{-}PEt_2)_2M(CO)_n$, where Cp = η^5-C_5H_5, NBD = norbornadiene, and M = Ni, Fe, Mo with n = 2, 3, 4, respectively. The singly bridged intermediate $Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$ was also prepared. The molecular structure of $Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$, determined by X-ray diffraction, consists of edge-shared pseudotetrahedral 16e Hf(IV) and pseudooctahedral 18e Mo(0) centers with a planar HfP_2Mo bridging unit and a Hf···Mo separation of 3.400 (1) Å. The complex crystallizes in space group C_{2h}^5—$P2_1/n$ (No. 14)—with four molecules in a cell of dimensions a = 13.315 (3) Å, b = 18.294 (6) Å, c = 10.103 (2) Å, and β = 91.21 (2)°.

The most widely used synthetic route[1] to diorganophosphido-bridged, early–late heterobimetallic complexes involves the deprotonation of metal-coordinated secondary phosphines and reaction of the resulting anions with a transition-metal halide. An example[2] relevant to this work is shown as follows.

$$cis\text{-}Mo(CO)_4(PRR'H)_2 \xrightarrow[\substack{(1)\ 2\ \text{equiv of } n\text{-BuLi} \\ (2)\ Cp_2MCl_2}]{Et_2O/-70\ °C} Cp_2M(\mu\text{-}PRR')_2Mo(CO)_4$$

R = R′ = Me; R = Ph, R′ = H, $SiMe_3$
M = Ti, Zr
Cp = η^5-C_5H_5

We recently reported[3] the synthesis and molecular structure of the neutral "metal-containing bis(phosphine)" $Cp_2Hf(PEt_2)_2$, which contains both single and double Hf–P bonds. We have used this and analogous complexes[4] to bind Ni(1,5-COD), $M(PR_3)$ (M

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Table I. Solution Infrared Spectral Data for (P P)M(CO)$_n$

complex	solvent	absorptions, cm^{-1}	ref
$Cp_2Hf(\mu\text{-}PEt_2)_2Ni(CO)_2$ (2)	*a*	1984 (vs), 1920 (vs)	*d*
$(DEPE)Ni(CO)_2$	*b*	1990 (vs), 1940 (vs)	14
$Cp_2Hf(\mu\text{-}PEt_2)_2Fe(CO)_3$ (3)	*c*	1980 (vs), 1917 (s), 1896 (vs)	*d*
$(DEPE)Fe(CO)_3$	*c*	1986 (vs), 1916 (s), 1901 (vs)	*d*
$Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$ (4)	*a*	2003 (s), 1912 (s), 1896 (s, sh), 1887 (vs)	*d*
$(DEPE)Mo(CO)_4$	*b*	2012 (s), 1909 (sh), 1891 (vs), 1873 (s)	13
$Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$ (5)	*a*	2023 (vs), 1942 (s), 1912 (vs), 1900 (vs)	*d*

[a] Toluene. [b] 1,2-Dichloroethane. [c] *n*-Hexane. [d] This work.

Table II. ^1H and $^{31}P\{^1H\}$ NMR Data for Complexes 1–5[a]

complex	^1H NMR δ			^{31}P NMR chem shift, ppm
	Cp^b	$CH_2{}^c$	$CH_3{}^d$	
$Cp_2Hf(PEt_2)_2$ (1)	5.48	1.93 (7.5, 3.1)	1.21 (7.5, 13.0)	107.7
$Cp_2Hf(\mu\text{-}PEt_2)_2M(CO)_n$				
2 (M = Ni, *n* = 2)	4.92	1.95 (7.3, 14.6), 1.76 (7.3, 14.6, 3.3)	1.35 (7.3, 14.1)	140.9
3 (M = Fe, *n* = 3)	4.86	1.99 (7.2, 14.4), 1.53 (7.2, 14.4, 3.2)	1.27 (7.2, 14.4)	160.8
4 (M = Mo, *n* = 4)	4.93	2.08 (7.3, 14.6), 1.78 (7.3, 14.6, 3.9)	1.30 (7.3, 14.3)	136.8
$Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$ (5)	5.48	1.99 (7.5, 7.5, 4 H), 1.99 (obs, 2 H), 1.62 (7.3, 14.6, 4.0, 2 H)	1.06 (7.3, 13.3), 0.86 (7.5, 13.3)	260.1, 20.3 (d, $^2J_{PP}$ = 23 Hz)

[a] Recorded on ca. 0.05 M C_6D_6 solutions. [b] Triplet with $^3J_{PH} = 1.5 \pm 0.5$ Hz (virtual triplet for 5). [c] Doublet of quartets or doublet of doublet of quartets; $^3J_{HH}$, $^2J_{PH}$, and, where applicable, $^4J_{PH}$ in parentheses (±0.5 Hz). [d] Doublet of triplets; $^3J_{HH}$ and $^3J_{PH}$ in parentheses (±0.5 Hz); obs = obscured by other resonances.

= Pd, Pt; R = Me, Ph, cyclohexyl),[5] and Rh(indenyl)[6] fragments, thus forming electronically unsaturated, early–late heterobimetallics. This report describes the binding of metal carbonyl fragments, the isolation of a singly bridged intermediate, and the X-ray structural determination of $Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$.

Experimental Section

All operations were conducted in a Vacuum Atmospheres glovebox with continuous nitrogen flush. Solvents were purified by standard techniques[7] and distilled from sodium– or potassium–benzophenone. $Mo(CO)_4(\eta^4$-norbornadiene),[8] $Fe(CO)_3(\eta^4$-benzylideneacetone),[9] and $LiPEt_2$[10] were prepared by literature methods. PEt_2H, $Ni(CO)_4$, bis(diethylphosphino)ethane (DEPE) (Strem), norbornadiene, benzylideneacetone, *n*-BuLi (Aldrich), $Fe_2(CO)_9$, $Mo(CO)_6$ (Pressure), and Cp_2HfCl_2 (Alfa) were used as received. NMR spectra were recorded on Bruker WM-400 (100.6-MHz ^{13}C NMR) and Nicolet NMC-200-NB (200-MHz ^1H and 81-MHz ^{31}P NMR) spectrometers. ^{13}C and ^{31}P NMR chemical shifts are positive downfield from external $SiMe_4$ and 85% H_3PO_4, respectively. Solution infrared spectra were recorded on a Perkin-Elmer 983 spectrometer using matched KBr cells with a 0.1-mm path length. Mass spectra were recorded on a VG 70-70 high-resolution mass spectrometer using electron-impact ionization, and elemental analyses were performed by Pascher Mikroanalytisches Labor, Bonn, West Germany. Infrared data are compiled in Table I, and Table II lists ^1H and ^{31}P NMR results.

$Cp_2Hf(PEt_2)_2$ (1). To a refluxing solution of 7.59 g (20.0 mmol) of Cp_2HfCl_2 in 75 mL of THF was added a solution of 3.85 g (40.1 mmol) of $LiPEt_2$ in 100 mL of THF over 15 min. After a further 1 h at reflux, the solution was stirred at 25 °C for 16 h. The solvent was then removed in vacuo, the red residue extracted with 300 mL of boiling hexane, and the extract filtered to remove LiCl. Cooling the extract to −30 °C for 12 h yielded, after filtration, washing with 2 × 20 mL of cold pentane, and drying in vacuo, 6.78 g of red-orange crystals of **1**. Further crops brought the total yield to 7.74 g (80%); mp 101–105 °C. Anal. Calcd for $C_{18}H_{30}HfP_2$: C, 44.41; H, 6.21. Found: C, 44.52; H, 6.34. ^{13}C NMR (gated, C_6D_6, $^1J_{CH}$ in Hz in parentheses): δ 103.72 (174, $^2J_{CH}$ = 6 Hz, C_5H_5), 23.85 (128, J_{CP} = 5 Hz, CH_2 of PEt_2), 16.23 (126, CH_3 of PEt_2).

$Cp_2Hf(\mu\text{-}PEt_2)_2Ni(CO)_2$ (2). To a solution of 2.00 g (4.15 mmol) of $Cp_2Hf(PEt_2)_2$ in 50 mL of toluene was added 0.77 g (4.51 mmol) of $Ni(CO)_4$. The solution was stirred for 2 h and evaporated to dryness. The residue was extracted with 150 mL of boiling hexane, the extract filtered hot, and the filtrate concentrated to 50 mL and cooled to −30 °C for 14 h. The resulting yellow-orange crystals were filtered off, washed with 2 × 5 mL of cold pentane, and dried in vacuo, yielding 2.28 g (91%); mp 172–175 °C. Anal. Calcd for $C_{20}H_{30}HfNiO_2P_2$: C, 39.93; H, 5.03; Hf, 29.67; Ni, 9.76; P, 10.30. Found: C, 40.14; H, 5.04; Hf, 28.7; Ni, 9.31; P, 10.49.

$Cp_2Hf(\mu\text{-}PEt_2)_2Fe(CO)_3$ (3). (i) From $Fe_2(CO)_9$. To a gently refluxing solution of 370 mg (0.66 mmol) of $Cp_2Hf(PEt_2)_2$ in 50 mL of toluene was added 240 mg (0.66 mmol) of $Fe_2(CO)_9$ as a solid in small increments. After the solution was refluxed for 30 min, the solvent was evaporated in vacuo. The dark residue was extracted with 100 mL of hexane, the extract filtered, and the filtrate concentrated to ca. 50 mL, refiltered, and cooled to −30 °C for 14 h. The resulting yellow-orange crystals were filtered off, washed with 2 × 5 mL of cold pentane, and dried in vacuo, yielding 53 mg of **3**. A second crop brought the total yield to 185 mg (45%).

(ii) From $Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$ (5). A solution of 200 mg (0.31 mmol) of $Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$ in 10 mL of toluene was refluxed for 1 h. The solvent was removed in vacuo and the residue extracted with 50 mL of boiling hexane. Cooling to −30 °C for 3 days yielded 86 mg of orange crystals of **3** (44%), mp 139–140 °C. MS for $C_{21}H_{30}O_3P_2FeHf$: calcd, 628.0488; found, 628.0481.

$Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$ (4). A mixture of 2.0 g (4.12 mmol) of $Cp_2Hf(PEt_2)_2$ and 1.24 g (4.12 mmol) of $Mo(CO)_4(\eta^4$-norbornadiene) in 50 mL of THF was refluxed for 36 h. The solvent was then removed, the residue dried for 2 h in vacuo and taken up in 50 mL of toluene, the resulting mixture filtered, and the filtrate treated with 50 mL of hexane. After the filtrate was cooled to −30 °C for 14 h, the yellow precipitate was filtered off and recrystallized from boiling hexane, yielding 1.27 g of **4** (44%); mp 284–286 °C. Anal. Calcd for $C_{22}H_{30}HfMoO_4P_2$: C, 38.03; H, 4.35; P, 8.92. Found: C, 37.69; H, 4.26; P, 8.68.

$Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$ (5). To a solution of 635 mg (1.31 mmol) of $Cp_2Hf(PEt_2)_2$ in 100 mL of hexane was added 475 mg (1.31 mmol) of $Fe_2(CO)_9$ as a solid. After the mixture was stirred for 22 h, the resulting suspension was filtered off and extracted with 175 mL of boiling hexane and the extract concentrated to 25 mL. The resulting yellow crystals were filtered off, washed with cold pentane, and dried in vacuo, yielding 160 mg of **5**. Another crop of 112 mg from the original

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Table III. Summary of X-ray Diffraction Data

complex	$(\eta^5\text{-}C_5H_5)_2Hf[(\mu\text{-}P(C_2H_5)_2]_2\text{-}Mo(CO)_4$ (4)
formula	$C_{22}H_{30}HfMoO_4P_2$
fw	694.86
a, Å	13.315 (3)
b, Å	18.294 (6)
c, Å	10.103 (2)
β, deg	91.21 (2)
V, Å^3	2460 (2)
Z	4
ρ_{calcd}, g cm^{-3}	1.876
space group	C_{2h}^5; $P2_1/n$ (No. 14)
cryst dimens, mm	0.26 × 0.30 × 0.33
temp, °C	−100
radiatn	Mo Kα (0.710 69 Å) from graphite monochromator
μ, cm^{-1}	51.01
transmissn factors	0.881–0.998; av 0.933
2θ limits, deg	4.0–55.0
total no. of observns	5640
no. of unique data, $F_o^2 > 3\sigma(F_o^2)$	4479
final no. of variables	271
R	0.029
R_w	0.031

hexane filtrate brought the total yield of **5** to 379 mg (44%); mp 139–140 °C (converts into **3**). Anal. Calcd for $C_{22}H_{30}FeHfO_4P_2$: C, 40.36; H, 4.62; Fe, 8.53; Hf, 27.76; P, 9.46. Found: C, 40.40, 40.25; H, 4.75, 4.65; Fe, 8.31, 8.32; Hf, 26.5, 26.4; P, 9.52, 9.54.

Generation of Fe(CO)$_3$(DEPE). To a suspension of 374 mg (1.31 mmol) of $Fe(CO)_3(\eta^4$-benzylideneacetone) in 10 mL of hexane was added 275 mg (1.33 mmol) of bis(diethylphosphino)ethane in 10 mL of hexane. The mixture was stirred for 17 h and filtered and the filtrate evaporated in vacuo. The residue was characterized spectroscopically. ^{1}H NMR (C_6D_6): δ 1.36 (complex mult, 8 H, CH_2 of PEt_2), 1.01 (complex mult, 4 H, $-CH_2CH_2-$ of DEPE), 0.84 (d of t, $^3J_{PH}$ = 13.1 Hz, $^3J_{HH}$ = 7.6 Hz, 12 H, CH_3 of PEt_2). $^{31}P\{^1H\}$ NMR (C_6D_6): 95.3 ppm (s).

X-ray Data Collection and Structure Solution and Refinement. An amber yellow crystal of complex **4** was encapsulated in a glass capillary under N_2 and mounted on a Syntex P3 diffractometer. The crystal was shown to be suitable on the basis of scans having peak widths at half-height of 0.30° at −100 °C. Preliminary photographic examination revealed the space group and approximate cell dimensions. These and other crystallographic data are compiled in Table III. The cell constants shown were then refined on the basis of 50 reflections chosen from diverse regions of reciprocal space.

Intensity data were collected by using the ω-scan technique (1.2° scan range, 4.0–10° min^{-1}, total background time = scan time). The intensities of 4 standard reflections were monitored every 200 reflections and shown to vary insignificantly. The intensities of several reflections were measured at 10° increments about the diffraction vector, and an empirical correction for absorption thereby derived was applied to the full data set. The data were processed by using counting statistics and a p value of 0.02.[11]

The solution and refinement were accomplished by using local modifications of the SDP programs supplied by the Enraf-Nonius Corp. The Hf and Mo atoms were located in a Patterson synthesis, and the positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier syntheses and least-squares refinements. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where $w = 1/\sigma^2(F_o)$. The atomic scattering factors used were taken from the compilations of Cromer and Waber[12a] and the anomalous dispersion terms used are Cromer's.[12b] The H atoms were located and included as idealized, fixed contributions [d(CH) = 0.95 Å and B_H = 4.0 Å^2]. Final convergence was realized as shown in Table III, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$. Peaks corresponding to 1.60, 1.00, and 0.80 e Å^{-3} adjacent to the metal atoms were found in a final difference map.

Selected bond lengths and angles are collected in Table IV. Positional and thermal parameters for the non-hydrogen atoms are given in Table V. Positional and thermal parameters for the idealized hydrogen atoms (Table VI), general temperature factor expressions (Tables VII), and structure factor amplitudes (Table VIII) are available as supplementary material.

Results and Discussion

Synthesis and Characterization. The reaction of $Cp_2Hf(PEt_2)_2$ (**1**) with $Ni(CO)_4$, $Fe_2(CO)_9$, and (η^4-norbornadiene)$Mo(CO)_4$ affords the new heterobimetallic complexes **2–4**.

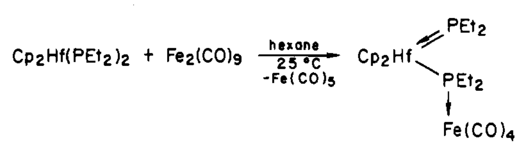
$$Cp_2Hf(PEt_2)_2 + Ni(CO)_4 \xrightarrow[-2CO]{\text{toluene}} \underset{\mathbf{2}}{Cp_2Hf(\mu\text{-}PEt_2)_2Ni(CO)_2}$$

$$Cp_2Hf(PEt_2)_2 + Fe_2(CO)_9 \xrightarrow[-Fe(CO)_5,\ CO]{\text{toluene, }\Delta} \underset{\mathbf{3}}{Cp_2Hf(\mu\text{-}PEt_2)_2Fe(CO)_3}$$

$$Cp_2Hf(PEt_2)_2 + (NBD)Mo(CO)_4 \xrightarrow[-NBD]{\text{THF, }\Delta} \underset{\mathbf{4}}{Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4}$$

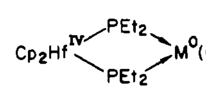
NBD = η^4-norbornadiene

The reaction of **1** with $Fe_2(CO)_9$ in hexane at 25 °C yields the singly bridged intermediate $Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4$ (**5**); thermolysis in toluene decarbonylates **5** to give **3**.

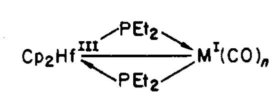


5

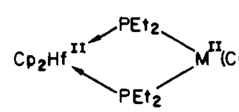
The new heterobimetallic complexes **2–5** are yellow to orange, air-sensitive crystalline solids, which were characterized by elemental analysis and IR, ^{1}H and ^{31}P NMR, and mass spectra. The IR spectra of complexes **2–4** (Table I) closely resemble those of their DEPE-substituted analogues,[13,14] suggesting that valence bond representation A is more apt than representation B or C.



A



B



C

Representation A is also chemially reasonable, as 16e Hf(IV) metal centers are common,[15] while Hf(II) or Hf(III) centers are not.[3,4,15,16] The characteristic ^{1}H NMR spectra (Table II) of **2–4** include a triplet resonance due to the cyclopentadienyl protons and multiplets for the two diastereotopic methylene protons[17] and the methyl protons of the diethylphosphide bridges. The ^{1}H NMR spectrum of **5** contains resonances due to bridging and terminal PEt_2 ligands. The $^{31}P\{^1H\}$ NMR spectrum of **5** consists of two doublets at 260.1 and 20.3 ppm, which we assign to the 3e donor terminal and bridging PEt_2 ligands, respectively.[18] The ^{31}P chemical shift of the PEt_2 bridges in the doubly bridged complexes

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(18) The 3e and 1e donor PCy_2 ligands in $Cp_2Hf(PCy_2)_2$ exhibit ^{31}P NMR chemical shifts (at −126 °C) of 270.2 and −15.3 ppm, respectively.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$ (4)

Hf---Mo	3.400 (1)		
Hf-P(1)	2.592 (1)	Mo-P(1)	2.538 (1)
Hf-P(2)	2.596 (1)	Mo-P(2)	2.534 (1)
Hf-C(10-14)	2.472-2.513 (5)	Hf-C(15-19)	2.484-2.506 (4)
Mo-C(1)	2.031 (4)	Mo-C(2)	1.984 (4)
Mo-C(4)	2.046 (4)	Mo-C(3)	1.990 (4)
P(1)-C(21)	1.847 (4)	P(2)-C(41)	1.849 (5)
P(1)-C(31)	1.841 (4)	P(2)-C(51)	1.850 (4)
C(1)-O(1)	1.143 (5)	C(2)-O(2)	1.152 (5)
C(4)-O(4)	1.130 (5)	C(3)-O(3)	1.151 (5)
C(10-13)-C(11-14)	1.378-1.395 (8)	C(15-18)-C(16-19)	1.398-1.412 (7)
C(*x*1)-C(*x*2) (*x* = 2-5)	1.508-1.527 (6)		
P(1)-Hf-P(2)	95.30 (3)	P(1)-Mo-P(2)	98.21 (3)
P(1)-Mo-C(1)	93.2 (1)	P(2)-Mo-C(1)	87.8 (1)
P(1)-Mo-C(2)	174.9 (1)	P(2)-Mo-C(2)	86.9 (1)
P(1)-Mo-C(3)	85.8 (1)	P(2)-Mo-C(3)	175.4 (1)
P(1)-Mo-C(4)	89.9 (1)	P(2)-Mo-C(4)	90.9 (1)
C(1)-Mo-C(2)	87.1 (2)	C(2)-Mo-C(3)	89.1 (2)
C(1)-Mo-C(3)	89.8 (2)	C(2)-Mo-C(4)	89.9 (2)
C(1)-Mo-C(4)	176.8 (2)	C(3)-Mo-C(4)	91.3 (2)
Hf-P(1)-Mo	83.01 (3)	Hf-P(2)-Mo	83.01 (3)
Hf-P(1)-C(21)	121.0 (1)	Hf-P(2)-C(41)	126.0 (2)
Hf-P(1)-C(31)	123.6 (1)	Hf-P(2)-C(51)	119.8 (2)
Mo-P(1)-C(21)	114.4 (1)	Mo-P(2)-C(41)	111.8 (1)
Mo-P(1)-C(31)	112.7 (1)	Mo-P(2)-C(51)	114.9 (2)
C(21)-P(1)-C(31)	101.7 (2)	C(41)-P(2)-C(51)	100.9 (2)
Mo-C(1)-O(1)	176.8 (4)	Mo-C(3)-O(3)	177.5 (4)
Mo-C(2)-O(2)	178.1 (4)	Mo-C(4)-O(4)	179.0 (4)
P(1)-C(21)-C(22)	116.5 (3)	P(2)-C(41)-C(42)	115.7 (3)
P(1)-C(31)-C(32)	114.5 (3)	P(2)-C(51)-C(52)	116.4 (3)
C-C-C[C(10)-C(14)]	107.1-108.6 (5)	C-C-C[C(15)-C(19)]	107.4-108.5 (4)

Table V. Positional and Isotropic Thermal Parameters for $Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$

Atom	x	y	z	B(A^2)	Atom	x	y	z	B(A^2)
HF	0.23582(1)	0.20176(1)	0.07846(2)	1.876(3)	C(13)	0.3937(5)	0.2575(4)	0.1745(7)	4.5(1)
MO	0.28308(3)	0.03624(2)	0.21952(4)	1.826(7)	C(14)	0.3319(5)	0.3139(3)	0.1326(7)	4.2(1)
P(1)	0.27915(9)	0.07546(7)	-0.0215(1)	1.91(2)	C(15)	0.0545(4)	0.1698(3)	0.0561(6)	3.2(1)
P(2)	0.2243(1)	0.15520(7)	0.3204(1)	2.28(2)	C(16)	0.0868(4)	0.1835(3)	-0.0737(6)	3.1(1)
O(1)	0.5066(3)	0.0904(2)	0.2732(5)	4.2(1)	C(17)	0.1138(4)	0.2575(3)	-0.0818(6)	3.2(1)
O(2)	0.2952(4)	-0.0276(2)	0.5074(4)	4.3(1)	C(18)	0.0960(4)	0.2909(3)	0.0415(6)	3.2(1)
O(3)	0.3664(3)	-0.1142(2)	0.1203(4)	3.59(9)	C(19)	0.0603(4)	0.2372(3)	0.1271(6)	3.1(1)
O(4)	0.0582(3)	-0.0202(3)	0.1905(6)	5.5(1)	C(21)	0.1871(4)	0.0256(3)	-0.1288(5)	2.7(1)
C(1)	0.4262(4)	0.0717(3)	0.2501(6)	2.6(1)	C(22)	0.2068(5)	-0.0558(3)	-0.1473(6)	3.8(1)
C(2)	0.2899(4)	-0.0031(3)	0.4025(5)	2.7(1)	C(31)	0.3975(4)	0.0559(3)	-0.1054(5)	2.5(1)
C(3)	0.3352(3)	-0.0587(3)	0.1537(5)	2.21(9)	C(32)	0.4004(4)	0.0820(3)	-0.2487(6)	3.1(1)
C(4)	0.1380(4)	0.0003(3)	0.2000(6)	2.9(1)	C(41)	0.3058(5)	0.1838(3)	0.4614(6)	3.3(1)
C(10)	0.3245(4)	0.3118(3)	-0.0053(7)	3.9(1)	C(42)	0.2819(5)	0.2572(4)	0.5209(7)	4.6(1)
C(11)	0.3783(4)	0.2513(4)	-0.0464(7)	4.3(1)	C(51)	0.1008(4)	0.1505(4)	0.4005(6)	3.6(1)
C(12)	0.4220(4)	0.2191(3)	0.0641(9)	4.7(2)	C(52)	0.0943(5)	0.1015(5)	0.5221(7)	5.7(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

2-4 is ca. 150 ppm; the shift to higher field for **5** is presumably due to the greater M-P-M angle in the latter.[19] In order to further define the electronic structure of **2-4**, we determined the molecular structure of **4** by X-ray diffraction.

Molecular Structure of $Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$ (4). The molecular structure of **4** shown in Figure 1 consists of edge-shared pseudotetrahedral Hf and pseudooctahedral Mo centers with a planar HfP_2Mo bridging unit.[20] The Hf-P distances (average 2.594 (1) Å) are midway between the Hf-P and Hf⇐P distances of 2.682 (1) and 2.488 (1) Å observed in $Cp_2Hf(PEt_2)_2$ (**1**).[3] The Mo-P distances (average 2.536 (1) Å) are comparable to those found for the metal-metal-bonded complex $[Mo(CO)_4(\mu\text{-}PEt_2)]_2$ (average 2.51 (1) Å).[21] The P-Hf-P angle of 95.3° is within

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(20) Distances from best HfP_2Mo plane (Å): Hf, 0.056; P(1), -0.057; P(2), -0.057; Mo, 0.059. The dihedral angle between HfP_2 and MoP_2 planes is 7.7°.

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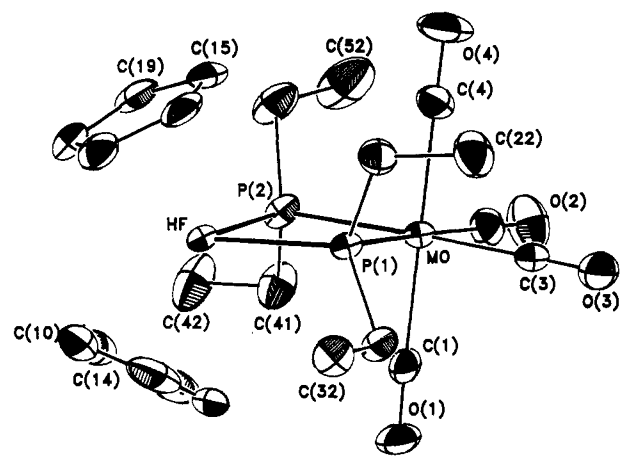

Figure 1. Perspective drawing of $Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$ (**4**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

the range found[22] (94–97°) for d^0 Cp_2MX_2 complexes and may be compared with P–Hf–P = 98.6 (1)° in $Cp_2Hf(PEt_2)_2$. The bulky Cp_2Hf vertex leads to large Hf–P–C angles to the PEt_2 bridges (ca. 122°). The intermediate[19] Hf–P–Mo angles of 83° result in a Hf···Mo separation of 3.400 (1) Å (cf. Mo–Mo = 3.057 (6) Å in $[Mo(CO)_4(\mu\text{-}PEt_2)]_2$). The influence of the bridge geometry on the observed metal–metal distance is exemplified by comparing the structure of **4** with that of $Cp_2Zr(\mu\text{-}PPh_2)_2W(CO)_4$.[23] As the covalent radii of Zr and Mo are very similar to those of Hf and W, the shorter metal–metal distance (Zr–W = 3.289 (1) Å) observed in the latter case must result primarily from substituting the PEt_2 with bulkier PPh_2 bridges.

Conclusion

The "metal-containing bis(phosphine)" $Cp_2Hf(PEt_2)_2$ binds metal carbonyl fragments to form new heterobimetallic complexes. The spectroscopic and X-ray structural results both suggest that these complexes contain adjacent 16e Hf(IV) and 18e M(0) centers. Reactivity studies on these and related electronically unsaturated heterobimetallics are presently under way.

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Registry No. **1**, 86013-26-5; **2**, 95552-78-6; **3**, 95589-49-4; **4**, 95552-79-7; **5**, 95552-80-0; $Fe(CO)_3$(DEPE), 95552-81-1; Cp_2HfCl_2, 12116-66-4; $LiPEt_2$, 19093-80-2; $Ni(CO)_4$, 13463-39-3; $Fe_2(CO)_9$, 15321-51-4; $Mo(CO)_4(\eta^4$-norbornadiene), 12146-37-1; $Fe(CO)_3(\eta^4$-benzylideneacetone), 38333-35-6.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters, idealized hydrogen atom positions, and observed and calculated structure amplitudes (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1062, and Battelle—C. F. Kettering Research Laboratory, Yellow Springs, Ohio 45387

Reactions of Cyclopropenes with Molybdenum(II) and Tungsten(II) Carbonyl Complexes: Formation of Coordinated Vinylketene

JOSEPH L. TEMPLETON,*[†] RICHARD S. HERRICK,[†] CATHERINE A. RUSIK,[†] CHARLES E. McKENNA,[‡] JOHN W. McDONALD,*[§] and WILLIAM E. NEWTON[§]

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Cyclopropene reacts with $Mo(CO)_2(S_2CNR_2)_2$, $Mo(CO)_2(S_2PR_2)_2$, $W(CO)_3(S_2CNR_2)_2$, and $W(CO)_2(PPh_3)(S_2CNR_2)_2$ to yield new complexes that are best formulated as $M(CO)(C_3H_4CO)(BB)_2$ (M = Mo, W). Analogous products form when 1-methylcyclopropene reacts with $W(CO)_3(S_2CNR_2)_2$. Infrared, ^1H NMR, and ^{13}C NMR spectroscopic techniques have been used to probe the mode of attachment of the newly formed vinylketene ligand, C_2H_3RCO (R = H, CH_3), which evidently results from cyclopropene ring opening and CO insertion.

Introduction

For several years we have been interested in the ability of low-valent molybdenum and tungsten dithiolate complexes to bind small molecules. The complexes $Mo(CO)_2(BB)_2$ (BB = S_2CNR_2, S_2PR_2) and $W(CO)_2L(S_2CNR_2)_2$ (L = CO, PPh_3) have been shown to react with acetylenes (including C_2H_2) to yield species of the form $M(CO)(RC_2R)(BB)_2$ (M = Mo, W)[1–4] and $M(RC_2R)_2(BB)_2$ (M = Mo).[2,5,6] NMR, structural, and reactivity data for these systems have been interpreted in terms of the alkynes behaving as formal four- and three-electron donors, respectively; a molecular orbital description[7] of these complexes has been published. Olefins either do not react with the above starting materials or form only weakly associated adducts that readily dissociate.[8]

Cyclopropene has properties intermediate between those of alkenes and alkynes,[9] and with this in mind, we have explored its

[†] The University of North Carolina.
[‡] University of Southern California.
[§] Battelle—C. F. Kettering Research Laboratory.

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