2514 *Organometallics* **1986**, *5*, 2514-2516

mmol). The mixture was allowed to warm slowly and stirred for 15 h at room temperature. The solvents were removed in vacuo, and the residue was extracted with pentane (50 mL). Concentrating the solution and cooling to −20 °C yielded 1.62 g (50%) of pale yellow crystals: mp 77 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.73 (s, 30 H, $Me_5\mathrm{C}_5$, $^3J_{^{117,119}\mathrm{Sn-H}}$ = 20.4 Hz), −0.02 (s, 3 H, $\mathrm{Me_2Sn}$, $^2J_{^{119}\mathrm{Sn-H}}$ = 44.6 Hz, $^2J_{^{117}\mathrm{Sn-H}}$ = 42.8 Hz); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 120.4 (Me_5C_5), 12.0 ($Me_5\mathrm{C}_5$), −8.4 ($\mathrm{Me_2Sn}$); ^{119}Sn{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 31; MS, *m/e* (relative intensity) 423 ($\mathrm{M^{\bullet +}}$, 1.1), 288 ($\mathrm{Me_5C_5SnMe(Me\text{-}}d_3)^+$, 80.7), 255 ($\mathrm{Me_5C_5Sn^+}$, 68.8), 135 ($\mathrm{Me_5C_5{}^+}$, 100). Anal. Calcd for $\mathrm{C_{22}H_{33}D_3Sn}$ (422.24): C, 62.58; H (D), 9.31. Found: C, 62.61; H, 9.45.

Bis(η^1-pentamethylcyclopentadienyl)methyltin Chloride (6). Methyltin trichloride (27.9 g, 116 mmol) was added during 30 min to an ice-cooled suspension of lithium pentamethylcyclopentadienide, prepared from a solution of 31.6 g (232 mmol) of pentamethylcyclopentadiene in tetrahydrofuran (about 700 mL) and a 1.55 M solution of *n*-butyllithium in hexane (155 mL, 232 mmol). The clear yellow solution was stirred for 20 h. Removal of the solvents in vacuo and extraction of the residue with 250 mL of petroleum ether were followed by concentrating and cooling the solution to −30 °C to yield 22.3 g (44%) of yellow crystals: mp 82–90 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.76 (s, 30 H, $\mathrm{Me_5C_5}$, $^3J_{^{117,119}\mathrm{Sn-H}}$ = 28.5), −0.04 (s, 3 H, MeSn, $^2J_{^{117,119}\mathrm{Sn-H}}$ = 44.0 Hz); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 122.0 ($\mathrm{Me_5C_5}$), 11.9 ($Me_5\mathrm{C}_5$), −5.9 (MeSn); ^{119}Sn{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 43; MS, *m/e* (relative intensity) 440 ($\mathrm{M^{\bullet +}}$, 1.8), 305 ($\mathrm{Me_5C_5Sn(Me)Cl^+}$, 9.5), 255 ($\mathrm{Me_5C_5Sn^+}$, 4.4), 135 ($\mathrm{Me_5C_5{}^+}$, 100). Anal. Calcd for $\mathrm{C_{21}H_{33}SnCl}$ (439.64): C, 57.37; H, 7.56. Found: C, 57.65; H, 7.60.

Reduction of 6 with Dilithium Cyclooctatetraenide. A solution of **6** (5.36 g, 12.3 mmol) in tetrahydrofuran (20 mL) was treated at −50 °C with the reagent, prepared from lithium dispersion (170 mg, 24.5 mmol) and cyclooctatetraene (1.39 mL, 12.3 mmol) in tetrahydrofuran (25 mL). The green-brown mixture was allowed to warm slowly, and stirring was continued for 6 days. After removal of the solvent in vacuo, the residue was extracted with 50 mL of petroleum ether. Concentrating the solution and cooling to −20 °C yielded a crude product. Recrystallization from pentane (cooling to −80 °C required) gave 529 mg (22%) of decamethylstannocene; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.10 (s, $^3J_{^{117,119}\mathrm{Sn-H}}$ = 3.6 Hz); ^{119}Sn{^{1}H} NMR ($\mathrm{CDCl_3}$) δ −2141. Anal. Calcd for $\mathrm{C_{20}H_{30}Sn}$ (389.15): C, 61.72; H, 7.77. Found: C, 61.50; H, 7.82.

Acknowledgment. We express our thanks to F. X. Kohl for valuable discussions during preparation of the manuscript.

Registry No. 1, 68757-81-3; 2, 41823-72-7; 4, 104834-02-8; 5, 104807-97-8; 6, 104807-98-9; [bis(trimethylsilyl)methyl]lithium, 41823-71-6; methyllithium, 917-54-4; *n*-butyllithium, 109-72-8; lithium pentamethylcyclopentadienide, 51905-34-1; dilithium cyclooctatetraenide, 37609-69-1; methyltin trichloride, 993-16-8.

Chemistry of Oxophilic Transition Metals. 2.[†,‡] Novel Derivatives of "Titanocene" and "Zirconocene"

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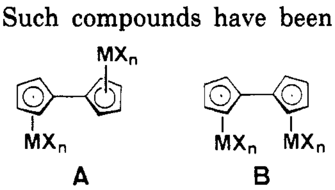
Reduction of dichlorobis(η^5-cyclopentadienyl)titanium(IV) (**3**) with 1.5 equiv of sodium amalgam (Na/Hg) gives the dinuclear η^5:η^5-fulvalene complex **4** of composition $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Ti}(\mu\text{-}\mathrm{Cl})]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}\mathrm{C_{10}H_8})$ and the "titanocene" **5** in 40% yield each; both compounds represent Ti(III) species. The chloro-bridged complex **4** undergoes quick oxidation upon exposure to air, thus yielding the Ti(IV) derivative $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{TiCl}]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}\mathrm{C_{10}H_8})(\mu\text{-}\mathrm{O})$ (**6**). Reduction of **4** with lithium triethylhydridoboranate cleanly gives "titanocene" **5**, with the latter compound representing a good starting material for the synthesis of the sulfido-bridged fulvalene complex $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Ti}(\mu\text{-}\mathrm{S})]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}\mathrm{C_{10}H_8})$ (**7**). Compound **7** in turn undergoes a sulfur/oxygen exchange reaction when treated with molecular oxygen; in this case, the oxo-/sulfido-bridged derivative $[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Ti}]_2(\mu\text{-}\mathrm{O})(\mu\text{-}\mathrm{S})(\mu\text{-}\eta^5{:}\eta^5\text{-}\mathrm{C_{10}H_8})$ (**8**) is formed.

Introduction

The chemistry of organometallic compounds containing fulvalene ligands has seen a considerable development in the past few years. This particular ligand allows the design of dinuclear complexes in which the metals can be in trans or cis position to each other as shown in A and B, respectively. Such compounds have been proposed as models in organic synthesis, and they may be attractive as sources of active centers in various catalytic processes.



A

B

Three general synthetic procedures have been devised to prepare fulvalene complexes of transition metals: (i) coupling of cyclopentadienyl ligands,[1] (ii) reactions with the fulvalene dianion,[2] and (iii) reaction of dihydrofulvalene with metal carbonyls.[3] ^{1}H NMR spectroscopy provides a convenient tool of characterizing fulvalene compounds: the presence of a plane of symmetry through the C1–C1' bond in the fulvalene ligand gives rise to an $\mathrm{A_2B_2}$ spin system (sometimes AA'BB') which is observed as two triplets or pseudotriplets. When this plane of symmetry is absent, four multiplets of an ABCD spin system are rather observed.

Fulvalene complexes of the group IV (4^9) transition metals have been confined, until recently, to compounds

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[†] This paper is dedicated to Professor R. Usøn on the occasion of his 60th birthday.

[‡] For part 1 of this series, see ref 5.

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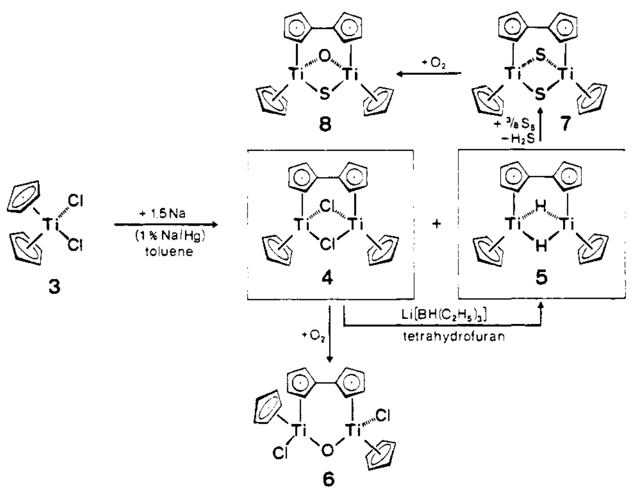
(3) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

0276-7333/86/2305-2514$01.50/0

Scheme I

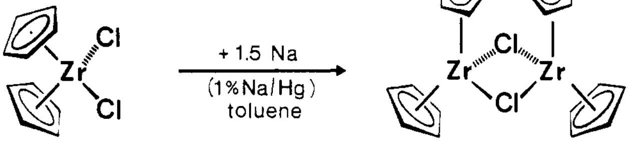


of titanium.[4] We have recently published the first well-characterized example of a dinuclear zirconium compound containing this ligand.[5] To our knowledge no fulvalene complex of hafnium is known up to now.

The synthesis of the zirconium compound **2** according to eq 1 provided an opportunity to compare its reactivity with that of the previously known titanium analogue. We report here an alternative, convenient preparation of the titanium complex **4** and its reaction with Li[BHEt$_3$] and oxygen. We also describe the reaction of the "titanocene" species **5** with elemental sulfur.

Results and Discussion

(a) Synthesis of [(C$_5$H$_5$)M(μ-Cl)]$_2$(μ-η^5:η^5-C$_{10}$H$_8$) (M = Ti, Zr). Reduction of (η^5-C$_5$H$_5$)$_2$ZrCl$_2$ (**1**) in toluene with sodium amalgam (1.0%) containing 1.5 molar equiv of sodium gives a high yield (75%) of a dark red solid characterized as the μ-η^5:η^5-fulvalene complex **2** (eq 1).[5]



1 **2**

Under the same conditions the reaction with the titanium analogue (η^5-C$_5$H$_5$)$_2$TiCl$_2$ (**3**) proceeds differently, giving a mixture of compound **4** in 40% yield and the "titanocene" **5** in 40% yield (Scheme I).

Both products can be conveniently purified since **5** is extractable with a *n*-hexane/diethyl ether mixture leaving **4** as the *only* organometallic species in the residue. This procedure is more convenient that the literature preparation of **4** which requires treatment of "titanocene" **5** with HCl.[4a,g] If an excess of the reducing agent is used, then the only organometallic species obtained is the green titanocene species **5**. It is interesting to note that under slightly different conditions, e.g., reduction with potassium instead of sodium amalgam, compound **5** of composition [{(C$_5$H$_5$)Ti}$_2$(μ-Cl)(μ-H)(μ-η^5:η^5-C$_{10}$H$_8$)] is obtained.[4f]

(b) Reaction of [(C$_5$H$_5$)M(μ-Cl)]$_2$(μ-η^5:η^5-C$_{10}$H$_8$) (M = Ti, Zr) with a Hydridoboranate Reducing Agent. Complex **4** reacts according to Scheme I with Li[BHEt$_3$] in tetrahydrofuran with gas evolution to give the "titanocene" **5** in quantitative yield. By way of contrast, the analogous zirconium derivative **2** reacts with Li[BHEt$_3$] to give a product which does not contain a fulvalene ligand. The ^{1}H NMR spectrum of the product shows a broad signal centred at δ 6 which is similar in appearance to the signals observed for the species obtained from the reduction of (η^5-C$_5$H$_5$)$_2$ZrCl$_2$ with excess sodium amalgam (so-called "zirconocene").[6] This species has not been fully characterized, but Schwartz et al.[7] have suggested that the reduced species contains {Zr$_2$(μ-η^1:η^5-C$_5$H$_4$)$_2$} units.

(c) Reactions of [(C$_5$H$_5$)M(μ-Cl)]$_2$(μ-η^5:η^5-C$_{10}$H$_8$) with Oxygen. Complex **2** is known to react rapidly with oxygen to give the μ-oxo complex of composition [{(C$_5$H$_4$)ZrCl}$_2$(μ-O)(μ-η^5:η^5-C$_{10}$H$_8$) which has been characterized by X-ray crystallography, as we have reported recently.[5] Complex **4** reacts with oxygen in an entirely similar way to give the analogous compound **6** (Scheme I). The mass spectrum of this complex confirms its dinuclear structure. The ^{1}H NMR spectrum (CDCl$_3$) shows a singlet for the protons of the cyclopentadienyl ligands at δ 6.19 and four multiplets for the protons of the fulvalene ligand at δ 5.67, 6.23, 6.51, and 6.75 (ABCD spin system). In the ^{13}C{^{1}H} NMR spectrum the carbon resonances due to the η^5-C$_5$H$_5$ ligands are found at δ 116.5 as a singlet and the C$_{1-5}$ carbon atoms for the fulvalene ligand are located at δ 103.5, 113.6, 115.4, 120.2, and 127.9 (five singlets). The NMR data are very similar to those of the μ-oxo complex of zirconium;[5] hence the titanium derivative **6** must have a similar structure with the oxo and fulvalene ligands bridging the two titanium atoms and the cyclopentadienyl and chloride ligands in trans positions with respect to the Ti$_2$O core structure. Attempts at obtaining crystals for an X-ray diffraction study are in progress.

(d) Reaction of "Titanocene" with Sulfur. The reactions of titanocene with hydrochloric acid and water have previously been described to give the chloro-bridged derivative **5** and [{(C$_5$H$_5$)Ti}$_2$(μ-OH)(μ-η^5:η^5-C$_{10}$H$_8$), respectively.[4a,c,g]

We have now examined the reaction of "titanocene" with sulfur and have found that addition of 3 equiv of sulfur to an ethereal solution of "titanocene" **5** produces almost immediately gas evolution (identified as H$_2$S) which is finished after approximately 5 min, followed by precipitation of a dark brown solid. This residue may be extracted with tetrahydrofuran to give the pure compound **7** in 60% yield (Scheme I).

The mass spectrum of **7** is consistent with the proposed dinuclear structure [m/z 418 (M$^+$)]. In the ^{1}H NMR spectrum (CDCl$_3$) the cyclopentadienyl protons are observed as a singlet at δ 6.16 while the protons of the fulvalene ligand give rise to two multiplets at δ 5.82 and 6.04 (J_{obsd} = 2.8 Hz). Integration of the observed signals gives an intensity ratio of 10/4/4 (270 MHz, C$_6$D$_6$, +28 °C): δ 5.91 (s, 10 H, C$_5$H$_5$), 5.14 (t, 4 H, C$_5$H$_4$), 5.97 (t, 4 H, C$_5$H$_4$, J_{obsd} = 2.8 Hz).

The ^{13}C{^{1}H} NMR spectrum shows the resonance of the cyclopentadienyl carbon atoms as a singlet at δ 110.5 whereas the resonance of the carbon atoms of the fulvalene ligand are observed at δ 106.5, 110.8 (C$_{2-5}$), and 113.6 (C$_1$).

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[4] (a) Brintzinger, H. H.; Bercaw, J. *J. Am. Chem. Soc.* **1970**, *92*, 6182. (b) Davison, A.; Wreford, S. S. *Ibid.* **1974**, *96*, 3017. Guggenberger, L. J.; Tebbe, F. N. *Ibid.* **1973**, *95*, 7870. (c) *Ibid.* **1976**, *98*, 4137. (e) Olthof, G. J. *J. Organomet. Chem.* **1977**, *128*, 367. (f) Perevalova, E. G.; Urazowski, J. F.; Lemenovski, B. A.; Slovokhotov, Y. L.; Struchkov, Y. T. *Ibid.* **1985**, *289*, 319. (g) Salzmann, J. J.; Mosimann, P. *Helv. Chim. Acta* **1967**, *50*, 1831.

[5] Ashworth, T. V.; Cuenca, T.; Herdtweck, E.; Herrmann, W. A. *Angew. Chem.* **1986**, *98*, 278; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 289.

[6] Pez, G. P. *Adv. Organomet. Chem.* **1981**, *19*, 1.

[7] Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481.

As in the case of the chloro-bridged compound **2** the spectral data for **7** show that the molecule possesses a plane of symmetry through the C1–C1' bond of the fulvalene ligand and the two metal atoms, thus requiring the sulfur atoms to occupy coordination sites bridging the two titanium centers.

The sulfur derivative **7** is stable in a nitrogen or argon atmosphere, but in contact with air it decomposes immediately to give the μ-oxo derivative **8**. The ^{1}H NMR spectrum ($CDCl_3$) for this new compound consists of a singlet at δ 6.30 for the cyclopentadienyl protons and of four multiplets for the protons of the fulvalene ligands [δ 5.80 (m, 2 H), 6.34 (m, 2H), 6.62 (m, 2 H), 6.85 (m, 2 H)]. The ^{1}H NMR pattern is consistent with the replacement of a sulfur by an oxygen atom since the plane of symmetry in the starting compound is absent in the product.

This type of compounds with edge-bridging oxo and sulfido ligands are very rare in the organometallic chemistry of the group IV (4) transition metals, and there is evidence for only two compounds in the literature.[8]

Experimental Section

General Data. All experimental procedures were carried out under nitrogen either in standard Schlenk apparatus or in an automated glovebox (MB-200, Braun Co., Garching/Germany). NMR spectra were recorded with a JEOL FT-270 instrument, and mass spectra were obtained by using a Varian MAT A-300 instrument with inlet/sample chamber conditions (10^{-7} torr, 250 °C). Elemental analyses were obtained from our own microanalytical laboratories.

(1) Reaction of (η^5-C_5H_5)$_2$TiCl$_2$ with Sodium Amalgam. (η^5-C_5H_5)$_2$TiCl$_2$ (1.0 g, 4 mmol) was added to a mixture of toluene (50 mL) and Na/Hg amalgam (1%; 0.140 g of Na, 6 mmol), and the mixture was stirred overnight. The resultant dark brown reaction mixture was then heated under reflux for 1.5 h during which time it became dark purple. After removal of the solvent in vacuo, "titanocene" [(C_5H_5)Ti(μ-H)]$_2$(μ-η^5:η^5-$C_{10}H_8$) was obtained by extraction with a *n*-hexane/diethyl ether mixture (1/2). Evaporation of the extract gives the product as a dark green powder in a 0.30-g yield (40%). Extraction of the residue with THF gives compound **4**, after filtration, concentration and addition of *n*-hexane, as a purple powder; yield 350 mg (40%).

(2) Reaction of the Fulvalene Titanium Complex 4 with Lithium Triethylhydridoboranate. Addition of a 1 M solution of Li[BHEt$_3$] (2 mL) in tetrahydrofuran to a solution of [(η^5-C_5H_5)Ti(μ-Cl)]$_2$(μ-η^5:η^5-$C_{10}H_8$)]$_2$ (426 mg, 1 mmol) in toluene (50 mL) resulted in an immediate color change from purple to dark green. Evaporation of the solvent in vacuo followed by extraction of the residue with *n*-hexane/diethyl ether (1/2) gives [(η^5-C_5H_5)Ti(μ-H)(μ-η^1:η^5-C_5H_4)]$_2$ as a dark green powder after concentration and cooling of the extract; yield 250 mg (85%).

(3) Reaction of the Fulvalene Zirconium Complex 2 with Lithium Triethylhydridoboranate. Addition of a 1 M solution of Li[BHEt$_3$] (2 mL) in tetrahydrofuran to solution of **2** (510 mg, 1 mmol) in toluene resulted in precipitation of lithium chloride and a slight darkening of the reaction mixture over several hours. Evaporation of the solvent in vacuo, followed by extraction with toluene, gives a dark purple solid which was characterized as the so-called "zirconocene" by NMR comparison of it NMR spectrum with an authentic sample.

(4) Reaction of the Fulvalene Titanium Complex 4 with Elemental Oxygen. A stream of pure, dry oxygen gas was passed through a solution of **4** (426 mg, 1 mmol) in toluene (50 mL) for several minutes. The pale yellow precipitate that formed was filtered and recrystallized from chloroform/*n*-hexane to give the product as a powder; yield 370 mg (85%). Anal. Calcd for $C_{20}H_{18}OCl_2Ti_2$: C, 54.44; H, 4.11; Cl, 16.07. Found: C, 54.23; H, 4.50; Cl, 15.73. IR [KBr, ν(TiOTi) cm^{-1}]: 734. EI-MS: *m/e* 375 (M − Cp$^+$).

(5) Reaction of the Fulvalene Titanium Complex 4 with Elemental Sulfur. A solution of **4** (356 mg, 1 mmol) in diethyl ether (50 mL) was treated with elemental sulfur (100 mg, 3 mmol). After gas evolution (H_2S) had ceased (5 min), the dark brown solid was filtered and recrystallized from tetrahydrofuran/*n*-hexane to give the product **7** as a brown powder; yield 240 mg (60%). Anal. Calcd for $C_{20}H_{18}OSTi_2$: C, 57.40; H, 4.30; S, 15.10. Found: C, 59.33; H, 4.15. IR [KBr, ν(TiOTi), cm^{-1}]: 732.

(6) Reaction of Fulvalene Titanium Complex 7 with Elemental Oxygen. A solution of **7** (418 mg, 1 mmol) tetrahydrofuran was exposed to air for several hours. A color change from dark brown to yellow was observed. Evaporation of the solvent and recrystallization of the residue from chloroform gives the product **8** as a yellow powder; 300 mg (75%). Anal. Calcd for $C_{20}H_{18}OSTi_2$: C, 59.69; H, 4.51. Found: C, 60.33, H, 4.15. IR [KBr, ν(TiOTi), cm^{-1}]: 732.

Acknowledgment. This work was generously supported by the Alexander von Humboldt-Stiftung (fellowships T.C.A. and T.V.A.) and the HOECHST Aktiengesellschaft.

Registry No. **2**, 100946-29-0; **3**, 1271-19-8; **4**, 11078-01-6; **5**, 52676-23-0; **6**, 104761-08-2; **7**, 104761-09-3; **8**, 104761-10-6; [(C_5H_5)Zr(μ-H)]$_2$(μ-η^5:η^5-$C_{10}H_8$), 104761-11-7.

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(8) Tainturier, G.; Gautheron, B.; Fahim, M. *J. Organomet. Chem.* **1985**, *290*, C4.

(9) In this paper the periodic group notation in parentheses 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 groups 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.)

Organometallics 1986, *5*, 2517–2522 2517

Synthesis and Reactivity Studies of Phosphido-Bridged Heterobimetallic Cr–Os and Fe–Os Formyl Complexes

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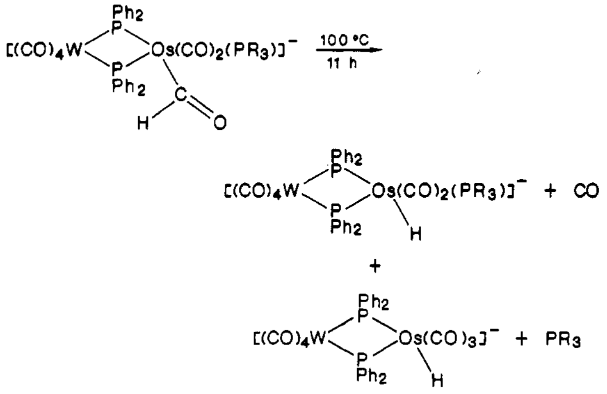
Received November 14, 1985

The new bimetallic complexes $(CO)_3Fe(\mu\text{-}PPh_2)_2Os(CO)_3$ (1), $(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_3$ (2), and $(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_3(PMePh_2)$ (3) have been prepared and spectroscopically characterized. Stable bimetallic formyl complexes $[(CO)_3Fe(\mu\text{-}PPh_2)_2Os(CO)_2(CHO)]^-$ (4) and $[(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_2(PMePh_2)(CHO)]^-$ (5) derive from 1 and 3 upon treatment with $Li[BHEt_3]$. Formyl complex 5 exists in two isomeric forms which appear to be geometrical isomers with the formyl ligand located in different coordination positions in the Os octahedral coordination sphere. Formyl complex 4 is unusual in that it is one of the few examples of a stable formyl complex with a metal–metal bond, and reasons for its unusual stability are discussed. Formyl complex 5 reacts with $[(CH_3)_3O]BF_4$ to give $(CO)_4Cr(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CH(OMe))Os(CO)_2(PMePh_2)$ (8) containing the μ-$PPh_2CH(OMe)$ ligand which derives from coupling of phosphide and methoxycarbene ligands, the latter being formed by methylation of the formyl oxygen.

In the course of our studies directed toward the preparation and reactions of binuclear and polynuclear formyl complexes, we prepared the bimetallic formyl derivatives $[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2(PR_3)]^-$ which were unusually stable.[1] For example, the $PMePh_2$ derivative required ~11 h at 110 °C for complete conversion to the corresponding hydride complex (eq 1). This unusual stability was attributed to the absence of a metal–metal bond in the initial formyl complex as well as to the inertness of the osmium center toward ligand loss. In other work, we have shown that the presence of metal–metal bonds can markedly limit the stability of formyl and acyl derivatives since metal–metal bond cleavage provides an easy access to the open coordination site needed for deinsertion.[2]



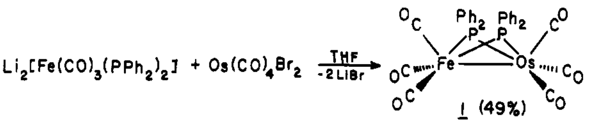
(1)

We describe herein the preparation and properties of bimetallic Fe–Os and Cr–Os formyl complexes similar to the W–Os formyl complex in eq 1, all with the formyl ligand bound to Os. These allow an assessment of the effect of the nature of the adjacent metal on the stability of the Os–formyl, and the Fe–Os complex has given an example of a stable formyl complex which has a metal–metal bond. The unusual stability of this derivative is rationalized on the basis of the overall geometry of the $M_2(\mu\text{-}PPh_2)_2$ core and the relative Fe–Os bond strength.

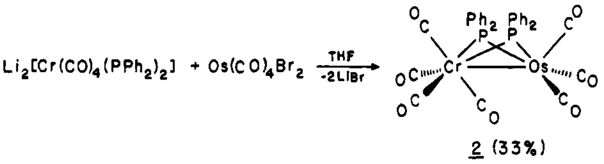
Results

Preparation and Characterization of $(CO)_3Fe(\mu\text{-}PPh_2)_2Os(CO)_3$ (1) $(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_3$ (2) and $(CO)_4Cr(\mu\text{-}PPh_2)_2Os(CO)_3PMePh_2$ (3).

The title complexes 1 and 2 were prepared by using the bridge-assisted synthetic routes[3] outlined in eq 2 and 3 which are analogous to the synthesis of $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_3$ reported earlier.[1] Both complexes 1 and 2 were isolated in pure form and have been spectroscopically characterized. NMR data (^{31}P, ^1H) for these and all the new compounds described herein are summarized in Table I. Both 1 and 2 show single downfield resonances in their $^{31}P\{^1H\}$ NMR spectra assigned to equivalent μ-PPh_2 ligands. The downfield positions imply the presence of a metal-metal



1 (49%)
(2)



2 (33%)
(3)

Table I. ^{31}P and ^1H NMR Data at 22 °C[a]

compd	$\delta(P_\mu)$	$\delta(P_{Os})$	$J_{P_\mu\text{-}P_\mu}$	$J_{P_\mu\text{-}P_M}$	$\delta(H)$	$J_{^1H\text{-}^{31}P}$
1	81.5 (s)					
2	197.4 (s)					
3	−79.6 (dd)	−27.0 (d)	10.3	88.6		
	−89.5 (d)					
4[b]	107.0 (d)		72.8		14.9 (dd)	18.8
	72.4 (d)					24.5
5a	−69.6 (dd)	−18.9 (dd)	45.0	107.3	15.3 (dd)	4.9
	−96.0 (dd)			11.4		24.9
5b	−70.2 (m)	−16.8 (dd)	7.3	135.0	15.4 (m)	
	−90.1 (dd)			11.4		
6	−91.7 (s)				−3.2 (t)	15
7	−88.3 (dd)	−11.0 (dd)	6.5	141.9	−3.6 (ddd)	10, 18
	−89.0 (dd)			12.5		24
8	41.0 (dd)	−2.7 (d)	7.4			
	111.6 (d)			10.2		

[a] Solvents used: C_6D_6 (**1**, **2**, **8**), CD_2Cl_2 (**3**), THF-d_8 (**4**–**6**), and $(CD_3)_2SO$ (**7**). *J* values in Hz. [b] ^{31}P, −80 °C; ^1H, −100 °C.

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