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Tridentate Coordination Modes of Functionalized Titanocene Thiolates. Crystal Structure of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-P-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-SPh})_2\text{W(CO)}_3]$

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Mixed monosubstituted cyclopentadienyl Ti(IV) derivatives $[(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti(SPh)}_2]$ (R = PPh_2, $\text{Ph}_2\text{P{=}O}$, $\text{Ph}_2\text{P{=}S}$) react with carbonylmetal fragments of group 6 to generate heterodinuclear compounds $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-P-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-SPh})_2\text{M(CO)}_3]$, $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{SPh})\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-P-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-SPh})\text{M(CO)}_4]$, $[(\eta^5\text{-C}_5\text{H}_4\text{P(E)Ph}_2)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu\text{-SPh})_2\text{M(CO)}_4]$ (M = Mo, W; E = O, S) and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-E-C}_5\text{H}_4\text{P(E)Ph}_2)(\mu\text{-SPh})_2\text{M(CO)}_3]$ (M = Mo, W; E = S or M = Mo, E = O). All complexes have been characterized by spectroscopic data. The crystal structure of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-P-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-SPh})_2\text{W(CO)}_3]$ has been determined by X-ray diffraction techniques, and it was confirmed that the titanium precursor acts as a tridentate metalloligand. The complex crystallizes in the orthorhombic system in space group $Pna2_1$; $a = 23.081(2)$ Å, $b = 14.3046(9)$ Å, $c = 11.6892(8)$ Å; $Z = 4$.

Introduction

Studies carried out on compounds containing SR ligands have revealed a rich chemistry, arising from the ability of the thiolate group to bridge a wide variety of metal centers.[1] In particular for titanium(IV), the capacity of titanocene thiolate derivatives to act as chelate ligands has been well established, specifically through the sulfur atoms in the absence of additional donor groups in the complex.[2] Following this idea, the functionalization of the cyclopentadienyl rings with donor groups might provide new coordination modes for the corresponding species $[(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti(SR}')_2]$. Indeed, in the last years we have reported a series of heterobi- and heterotrimetallic species showing different chelation modes by using $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Ti(SR)}_2]$ (R = Ph, Et) derivatives as bidentate ligands.[3]

Much less effort has been devoted to the synthesis of new titanium(IV) complexes incorporating mixed monosubstituted cyclopentadienyl rings.[4] Among them, the only examples available in the literature of titanocene thiolate metalloligands of this type have been recently prepared by us.[5] The instability in solution of the species $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Ti(SR)}_2]$ comparing to related derivatives $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti(SR)}_2]$, encouraged us to synthesize the new complex $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti(SPh)}_2]$ in an attempt to enhance the stability in solution while maintaining the ability of the PPh_2 group to bind other metal. Furthermore, the ease of oxidation of the P atom in tertiary phosphines coupled with the scarce data on the coordination chemistry of oxo- or thiophosphorylcyclopentadienyl ligands[6] has also prompted us recently to synthesize the new complexes $[(\eta^5\text{-C}_5\text{H}_4\text{P(E)Ph}_2)(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Ti(SPh)}_2]$ (R = SiMe_3, P(E)Ph_2; E = O,S).[5]

Following our research project on the synthesis of heteronuclear complexes using thiolate derivatives of titanocene as metalloligands we wish to report here the reactions of the complexes $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti(SPh)}_2]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{P(E)Ph}_2)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti(SPh)}_2]$ (E = O, S) with M(CO)_4 and M(CO)_3 (M = Mo, W) fragments.

Experimental Section

All preparative reactions, chromatography and manipulations were carried out under on atmosphere of argon using standard Schlenk techniques.[7] Solvents were dried and distilled under argon before use according to standard procedures.[8] The syntheses of $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti(SPh)}_2]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{P(E)Ph}_2)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti(SPh)}_2]$ (E =O, S) have been recently reported.[5] $[\text{Mo(CO)}_4(\text{NCMe})_2]$,[9] $[\text{M(CO)}_3(\text{NCMe})_3]$[10] (M = Mo, W), $[\text{Mo(CO)}_4(\text{nbd})]$,[11] and $[\text{W(CO)}_4(\text{nbd})]$[12] (nbd = bicyclo[2.2.1]hepta-2,5-diene or 2,5-norbornadiene) were prepared according to literature methods. Microanalyses were

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determined with a Perkin-Elmer 2400 microanalyzer, mass spectra on a VG Autospec instrument, and infrared spectra on a Perkin-Elmer 1600 FT spectrophotometer. NMR spectra were recorded on Bruker AMX-300 and -400 instruments, with chemical shifts reported in ppm relative to external standards (TMS for ^{1}H NMR and H_3PO_4 for ^{31}P NMR).

Syntheses. $[(\eta^5\text{-}C_5H_4SiMe_3)(SPh)Ti(\mu\text{-}\eta^5\text{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SPh)M(CO)_4]$, M = W (1), Mo (2). A solid sample of $[W(CO)_4(NCMe)_2]$ (0.21 g, 0.57 mmol) was added to a solution of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (0.25 g, 0.38 mmol) in toluene (20 cm^3) at room temperature, and the resulting mixture was stirred for 1 h. The solvent was then evaporated, and the resulting residue was chromatographed on silica gel 100. Elution with *n*-hexane−toluene (1:2) afforded a green band corresponding to compound **1**, which was recrystallized from *n*-hexane−diethyl ether (0.17 g, 48%). Complex **2** was isolated following the same procedure and 3 h of reaction (yield 83%).

Data for **1**: Found C, 52.03; H, 4.34. $C_{41}H_{37}O_4PS_2SiTiW$ requires C, 51.93; H, 4.08. ν_{max} (toluene solution) 2009 (m), 1915 (m), 1885 (s), 1867 (m) (CO) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.85−7.20 (20H, m, C_6H_5), 6.96 (1H, m, $C_5H_4PPh_2$), 6.52 (3H, m, $C_5H_4PPh_2$, $C_5H_4SiMe_3$), 5.66 (1H, m, $C_5H_4SiMe_3$), 5.53 (1H, m, $C_5H_4SiMe_3$), 5.50 (1H, m, $C_5H_4SiMe_3$), 5.45 (1H, m, $C_5H_4PPh_2$), 0.19 (9H, s, CH_3) ppm; (−30 °C, CD_2Cl_2) δ 7.90−7.20 (20H, m, C_6H_5), 6.80 (1H, m, $C_5H_4PPh_2$), 6.60 (1H, m, $C_5H_4PPh_2$), 6.51 (1H, m, $C_5H_4PPh_2$), 6.49 (1H, m, $C_5H_4SiMe_3$), 5.81 (1H, q, $C_5H_4SiMe_3$, $J = 2.0$ Hz), 5.65 (1H, q, $C_5H_4SiMe_3$, $J = 2.6$ Hz), 5.49 (1H, quint, $C_5H_4SiMe_3$, $J = 2.4$ Hz), 5.42 (1H, m, $C_5H_4PPh_2$), 0.21 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 28.8 (s, *P*Ph$_2$, $J_{W-P} = 251$ Hz) ppm; (−30 °C, CD_2Cl_2) δ 27.1 (s, *P*Ph$_2$, $J_{W-P} = 247$ Hz) ppm. FAB-MS: $m/z = 948$ (M$^+$), 920 (M$^+$ − CO), 864 (M$^+$ − 3CO), 836 (M$^+$ − 4CO).

Data for **2**: Found C, 56.91; H, 4.31. $C_{41}H_{37}MoO_4PS_2SiTi$ requires C, 57.23; H, 4.30. ν_{max} (toluene solution) 2015 (m), 1923 (m), 1898 (s), 1872 (m) (CO) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.90−7.15 (20H, m, C_6H_5), 6.95 (1H, m, $C_5H_4PPh_2$), 6.52 (3H, m, $C_5H_4PPh_2$, $C_5H_4SiMe_3$), 5.63 (1H, m, $C_5H_4SiMe_3$), 5.47 (2H, m, $C_5H_4SiMe_3$), 5.40 (1H, m, $C_5H_4PPh_2$), 0.19 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 38.4 (s, *P*Ph$_2$) ppm. FAB-MS: $m/z = 860$ (M$^+$), 832 (M$^+$ − CO), 776 (M$^+$ − 3CO), 748 (M$^+$ − 4CO).

$[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5\text{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SPh)_2M(CO)_3]$, M = W (3), Mo (4). A dichloromethane solution (10 cm^3) of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (0.30 g, 0.46 mmol) was added to another dichloromethane solution (20 cm^3) of $[W(CO)_3(NCMe)_3]$ (0.30 g, 0.77 mmol) at room temperature. The resulting mixture was stirred for 2.5 h, and then the solvent was evaporated to dryness. The solid residue obtained was purified by chromatography on silica gel 100. Using *n*-hexane−toluene (2:1) as eluent a green band of complex **1** (trace amount) is obtained, and *n*-hexane−toluene (1:1) gave a purple band corresponding to **3** (0.27 g, 57%).

When the reaction was carried out with $[Mo(CO)_3(NCMe)_3]$ and worked up in a fashion similar to that described above a mixture of complexes **2** (trace amount) and **4** was obtained. However, all attempts to separate them failed, and complex **4** could only be characterized in solution.

Data for **3**: Found C, 54.18; H, 4.30. $C_{40}H_{37}O_3PS_2SiTiW \cdot 0.5C_6H_5\text{-}CH_3$ requires C, 54.05; H, 4.24. ν_{max} (dichloromethane solution) 1941 (s), 1879 (m), 1846 (m) (CO) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.59−7.14 (20H, m, C_6H_5), 5.69 (2H, m, $C_5H_4PPh_2$), 5.63 (2H, t, $J = 2.2$ Hz, $C_5H_4SiMe_3$), 5.50 (2H, m, $C_5H_4PPh_2$), 4.83 (2H, m, $C_5H_4SiMe_3$), 0.28 (9H, s, CH_3) ppm; (−70 °C, $CDCl_2$) δ 7.79−7.18 (40H, m, C_6H_5), 6.20 (2H, s, C_5H_4, *a* isomer), 5.91 (4H, s, C_5H_4, *b* isomer), 5.67 (2H, s, C_5H_4, *b* isomer), 5.20 (2H, s, C_5H_4, *a* isomer), 4.58 (2H, s, C_5H_4, *b* isomer), 4.55 (2H, s, C_5H_4, *a* isomer), 4.45 (2H, s, C_5H_4, *a* isomer), 0.31 (9H, s, CH_3, *a* isomer), 0.28 (9H, s, CH_3, *b* isomer) ppm (ratio *a*/*b* 1:9). $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ −3.5 (s, *P*Ph$_2$, $J_{W-P} = 216$ Hz) ppm; (−60 °C, CD_2Cl_2) δ 0.7 (s, *P*Ph$_2$, $J_{W-P} = 216$ Hz, *a* isomer), −5.7 (s, *P*Ph$_2$, $J_{W-P} = 216$ Hz, *b* isomer) ppm. FAB-MS: $m/z = 920$ (M$^+$), 864 (M$^+$ − 2CO), 836 (M$^+$ − 3CO).

Data for **4**: ν_{max} (dichloromethane solution) 1943 (s), 1888 (m), 1854 (m) (CO) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.60−7.10 (20H, m, C_6H_5), 5.64 (2H, m, $C_5H_4PPh_2$), 5.59 (2H, t, $J = 2.2$ Hz, $C_5H_4SiMe_3$), 5.46 (2H, m, $C_5H_4PPh_2$), 4.80 (2H, m, $C_5H_4SiMe_3$), 0.20 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 13.2 (s, *P*Ph$_2$) ppm.

Reaction of $[(\eta^5\text{-}C_5H_4P(E)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (E = S, O) and $[Mo(CO)_4(nbd)]$ in Toluene. A solution of complex $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (0.30 g, 0.43 mmol) in toluene (25 cm^3) was treated with $[Mo(CO)_4(nbd)]$ (0.13 g, 0.43 mmol) and stirred at room temperature. After 30 min the reaction led to a mixture of compounds $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}SPh)_2Mo(CO)_4]$ (**5**) and $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5\text{:}\kappa\text{-}S\text{-}C_5H_4P(S)Ph_2)(\mu\text{-}SPh)_2Mo(CO)_3]$ (**6**). All attempts to isolate **5** in pure form from the mixture have been unsuccessful, and a matching elemental analysis could not be obtained.

The same behavior was observed when the reaction was carried out with complex $[(\eta^5\text{-}C_5H_4P(O)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$, with compounds $[(\eta^5\text{-}C_5H_4P(O)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}SPh)_2Mo(CO)_4]$ (**7**) and $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5\text{:}\kappa\text{-}O\text{-}C_5H_4P(O)Ph_2)(\mu\text{-}SPh)_2Mo(CO)_3]$ (**8**) being detected in this case.

Data for **5**: ν_{max} (toluene solution) 2018 (m), 1947 (m), 1931 (s), 1912 (m) (CO) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.82−7.26 (20H, m, C_6H_5), 6.50 (2H, m, C_5H_4), 6.40 (2H, m, C_5H_4), 5.98 (2H, m, C_5H_4), 4.94 (2H, m, C_5H_4), 0.36 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 35.9 (s, *P*(S)Ph$_2$) ppm.

Data for **7**: ν_{max} (toluene solution) 2019 (m), 1950 (m), 1935 (s), 1911 (m) (CO) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.75−7.24 (20H, m, C_6H_5), 6.85 (2H, m, C_5H_4), 6.61 (2H, m, C_5H_4), 6.15 (2H, m, C_5H_4), 4.51 (2H, m, C_5H_4), 0.23 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 21.0 (s, *P*(O)Ph$_2$) ppm.

$[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5\text{:}\kappa\text{-}E\text{-}C_5H_4P(E)Ph_2)(\mu\text{-}SPh)_2M(CO)_3]$ [E = S, M = Mo (6); E = O, M = Mo (8); E = S, M = W (9)]. To a dichloromethane solution (20 cm^3) of $[Mo(CO)_3(NCMe)_3]$ (0.13 g, 0.44 mmol) at room temperature was added $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (0.25 g, 0.36 mmol), and the resulting solution was stirred for 15 min. After evaporation of the solvent to dryness the solid residue obtained was chromatographed on silica gel 100. Compound **6** was eluted from a mixture *n*-hexane−toluene (1:2) as a violet band. Recrystallization from *n*-hexane−toluene (1:1) at 0 °C afforded a violet solid (0.21 g, 70%). Complex **8** was isolated following the same procedure.

When the reaction was carried out using $[W(CO)_3(NCMe)_3]$ complex **9** was obtained. Elution from toluene−thf (5:1) and recrystallization from dichloromethane−methanol (1:1) at 0 °C yielded **9** as violet needles.

Data for **6**: Found C, 55.05; H, 4.48. $C_{40}H_{37}MoO_3PS_3SiTi$ requires C, 55.56; H, 4.31. ν_{max} (dichloromethane solution) 1951 (s), 1897 (m), 1809 (m) (CO) cm^{-1}; (KBr pellets) 634 (P═S) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.60−7.15 (20H, m, C_6H_5), 6.22 (2H, m, $C_5H_4PPh_2$), 5.83 (2H, m, $C_5H_4PPh_2$), 5.51 (2H, t, $J = 2.2$ Hz, $C_5H_4SiMe_3$), 4.87 (2H, t, $J = 2.2$ Hz, $C_5H_4SiMe_3$), 0.33 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 44.8 (s, *P*(S)Ph$_2$) ppm. FAB-MS: $m/z = 864$ (M$^+$), 808 (M$^+$ − 2CO), 780 (M$^+$ − 3CO).

Data for **8**: Yield 62%. Found C, 56.38; H, 4.22. $C_{40}H_{37}MoO_4PS_2SiTi$ requires C, 56.61; H, 4.39). ν_{max} (dichloromethane solution) 1947 (s), 1890 (m), 1804 (m) (CO) cm^{-1}; (KBr pellets) 1144 (P═O) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.62−7.16 (20H, m, C_6H_5), 5.99 (2H, m, $C_5H_4PPh_2$), 5.84 (2H, m, $C_5H_4PPh_2$), 5.55 (2H, t, $J = 2.2$ Hz, $C_5H_4SiMe_3$), 4.87 (2H, t, $J = 2.4$ Hz, $C_5H_4SiMe_3$), 0.20 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 38.6 (s, *P*(O)Ph$_2$) ppm. FAB-MS: $m/z = 848$ (M$^+$), 820 (M$^+$ − CO), 792 (M$^+$ − 2CO), 764 (M$^+$ − 3CO).

Data for **9**: Yield 65%. Found C, 48.63; H, 3.93. $C_{40}H_{37}O_3PS_3SiTiW \cdot CH_2Cl_2$ requires C, 48.78; H, 3.89). ν_{max} (dichloromethane solution) 1945 (s), 1887 (m), 1803 (m) (CO) cm^{-1}; (KBr pellets) 630 (P═S) cm^{-1}. ^{1}H NMR (room temperature, $CDCl_3$) δ 7.98−7.15 (20H, m, C_6H_5), 6.24 (2H, m, $C_5H_4PPh_2$), 5.81 (2H, m, $C_5H_4PPh_2$), 5.49 (2H, t, $J = 2.4$ Hz, $C_5H_4SiMe_3$), 4.87 (2H, t, $J = 2.4$ Hz, $C_5H_4SiMe_3$), 0.07

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Table 1. Crystallographic Data for **3**

empirical formula	$C_{40}H_{37}O_3PS_2SiTiW$	space group	$Pna2_1$
a, Å	23.081(2)	T, °C	20
b, Å	14.3046(9)	λ, Å	0.710 73
c, Å	11.6892(8)	ρ_{calcd}, mg m^{-3}	1.584
V, Å^3	3859.4 (4)	μ, mm^{-1}	3.402
Z	4	R1,[a] wR2[b] $[I < 2^{\sigma}(I)]$	0.0462, 0.1214
fw	920.63	R_{F_o}[a] $R_{wF_o^2}$[b] (all data)	0.0483, 0.1237

[a] $R_{F_o} = [\Sigma(|F_o| - |F_c|)]/\Sigma(|F_o|$. [b] $R_{wF_o^2} = \{[\Sigma(F_o^2 - F_c^2)]/\Sigma(F_o)^2\}^{1/2}$.

(9H, s, CH_3) ppm; (−60 °C, CD_2Cl_2) δ 7.61−7.20 (20H, m, C_6H_5), 6.39 (2H, m, $C_5\mathit{H}_4PPh_2$), 5.95 (2H, m, $C_5\mathit{H}_4PPh_2$), 5.65 (2H, t, $J = 2.3$ Hz, $C_5\mathit{H}_4SiMe_3$), 4.85 (2H, t, $J = 2.2$ Hz, $C_5\mathit{H}_4SiMe_3$), 0.01 (9H, s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (room temperature, $CDCl_3$) δ 46.0 (s, $\mathit{P}(S)Ph_2$) ppm; (−60 °C, CD_2Cl_2) δ 46.0 (s, $\mathit{P}(S)Ph_2$) ppm. FAB-MS: *m/z* 952 (M^+), 924 ($M^+ - CO$), 896 ($M^+ - 2CO$), 868 ($M^+ - 3CO$).

X-ray Structure Determination of Compound 3. A summary of the fundamental crystallographic data is given in Table 1. A dark red prismatic crystal was selected. The cell parameters were determined and refined from the values of 94 reflections. A quadrant of data was collected at 20 °C (Mo Kα radiation (λ = 0.710 73 Å); graphite monocromator) with a Siemens CCD diffractometer (sealed tube 2.4 kW) via two runs of 0.3° ω scans at different φ ($-15 \le h \le 24$, $-15 \le k \le 14$, $-3 \le l \le 13$; θ range 1.67−23.38°). The number of reflections collected was 8423. Intensities were corrected for absorption by applying SADABS program.[13] The maximum and minimum effective transmission factors were 0.112 and 0.037, respectively. The structure was solved by direct methods and least-squares refinement (based on F^2) with SHELXTL[14] using 3125 independent reflections. Hydrogen atoms were geometrically calculated and fixed. The final difference map was essentialy featuresless with the highest peak of 1.376 and the hole of −2.281 e Å^{-3}. The goodness of fit parameter on F^2 was 1.040.

Results and Discussion

Several examples of heteronuclear compounds formed by reaction of bis(cyclopentadienyl) bis(thiolate) derivatives of titanium (IV) and group 6 metal carbonyls are available in the literature;[3b,15] however, analogous complexes containing mixed monosubstituted rings are unknown.

By reaction of $[M(CO)_4(NCMe)_2]$ (M = W, Mo) and $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ at room temperature, the compounds $[(\eta^5\text{-}C_5H_4SiMe_3)(SPh)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SPh)M(CO)_4]$ [M = W (**1**), Mo (**2**)] have been obtained as green solids soluble in most common polar solvents.

The four CO stretching bands observed in the IR spectra at 2009, 1915, 1885, 1867 cm^{-1} (M = W) and 2015, 1923, 1898, 1872 cm^{-1} (M= Mo) support a *cis*-$M(CO)_4$ coordination, and they appear in the same range than those reported for other Ti−M (M = Mo, W) heteronuclear complexes bearing thiolate or cyclopentadienylphosphine bridges.[3b,16] The ^{31}P NMR spectra at room temperature for **1** and **2** display singlet resonances at 28.8 [$J(^{31}P-^{183}W)$ 251.1 Hz] and 38.4 ppm, respectively, strongly downfield shifted comparing with the starting material (−15.7 ppm). The evidence obtained from the $^{31}P\{^1H\}$ NMR and IR spectra suggests linkage of the $M(CO)_4$ fragment to the titanium through the P,S atoms.

In the room temperature ^1H NMR, both compounds exhibit a complex set of resonances for the cyclopentadienyl protons. Data reported for compound $[(SPh)_2Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)_2Mo(CO)_4]$[3b] indicate a downfield shift of the ring protons, while an S,S coordination results in an upfield shift in complexes $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}SR)_2Mo(CO)_4]$.[2b,17] The P,S coordination mode in compounds **1** and **2** is expected to provoke the two effects before mentioned. Furthermore, the presence around the titanium atom of two different rings as well as the coordination to the $M(CO)_4$ fragments of only one of the SPh groups makes the complexes chiral. The comparison of ^1H and $^1H\{^{31}P\}$ NMR spectra of complex **1** reveals the coupling of three $C_5H_4PPh_2$ ring protons to the phosphorus atom. The complete assignment of the resonances corresponding to each cyclopentadienyl ring was aided by a ^1H COSY experiment at −60 °C (Figure 1).

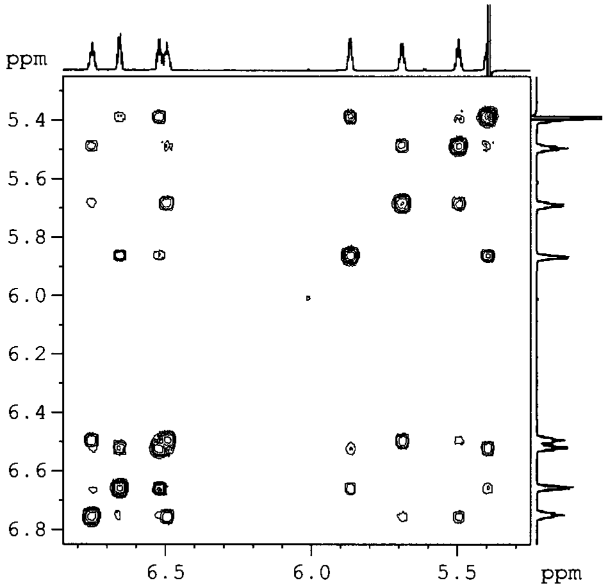

Figure 1. ^1H COSY spectrum of $[(\eta^5\text{-}C_5H_4SiMe_3)(SPh)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SPh)W(CO)_4]$ (**1**) in the cyclopentadienyl region at −60 °C in CD_2Cl_2.

The stereochemical nonrigidity in solution of SR ligands in these type of compounds may affords syn-anti isomers; however, the ^1H and ^{31}P NMR spectra of compound **1** at different temperatures show the presence of only one.

Although some carbonyl complexes of group 6 showing P,S,S or S,S,S coordination modes have been synthesized.[18] To our knowledge, only a few examples of metallocenes of group 4 have been reported to act as tridentate ligands bridging $M(CO)_3$ fragments through P,P,S or P,P,Cl atoms $[XM(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)_2(\mu\text{-}X)M'(CO)_3]$ [X = Cl, SMe; M = Ti, Zr; M′ = Mo, W].[19]

With these precedents in mind and due to the presence of three donor atoms in the titanium mononuclear precursor mentioned above, we have also studied its coordination chemistry toward group 6 tricarbonyl fragments.

Thus, when the reaction between $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ and $[M(CO)_3(NCMe)_3]$ (M = W, Mo) was carried out using toluene as solvent, mixtures of complexes **1** or **2** and $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SPh)_2M\text{-}$

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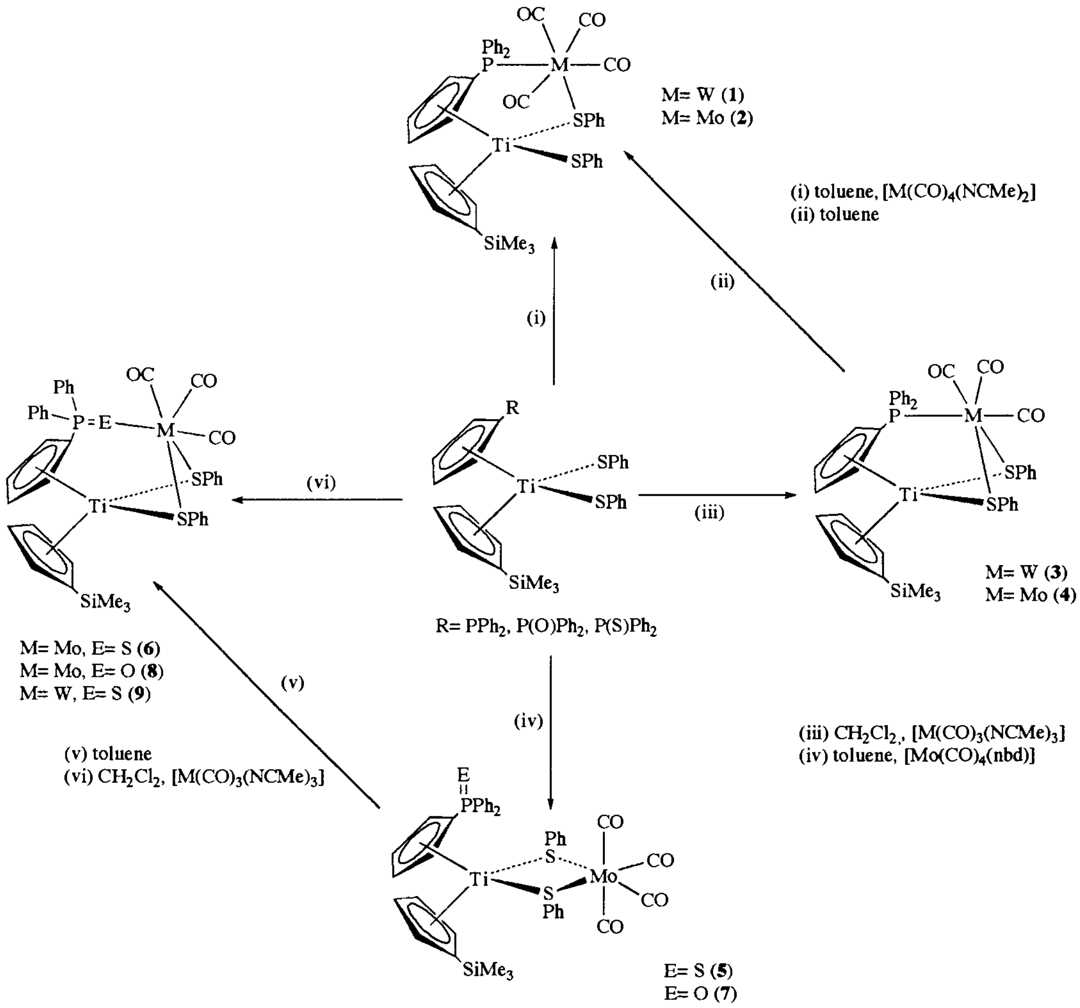
Scheme 1



$(CO)_3]$ [M = W (**3**), Mo (**4**)], as minor compounds, were obtained (Scheme 1). After several hours of stirring at room-temperature complexes **1** or **2** were the only species present in solution. This result indicates an initial P,S,S coordination of the tricarbonyl metal fragments and further conversion from this facial arrangement to a more stable *cis*-P,S-$[M(CO)_4]$ coordination mode. We believe that steric constraints imposed by the two bulky cyclopentadienyl rings could be responsible for the labilization of one M−S (M = W, Mo) bond and subsequent carbonylation.

However, we found that the use of dichlorometane instead of toluene in the above experiments allows to obtain **3** or **4** as the major compounds. Both complexes are formulated as dinuclear Ti−M (M = W, Mo) species with P,S,S bridges, which has been confirmed by X-ray diffraction study carried out for **3**.

The fac geometry for complex $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5\text{:}\kappa\text{-P-}C_5H_4PPh_2)(\mu\text{-SPh})_2W(CO)_3]$ is also supported by its IR spectrum. The carbonyl region shows a strong ν(CO) A_1 band at 1941 cm^{-1} and two bands of medium intensity at 1879 and 1846 cm^{-1} resulting from the splitting of the expected E band when the symmetry of the complex is lowered. This pattern is very similar to that reported for closely related compounds $[ClZr(\mu\text{-}\eta^5\text{:}\kappa\text{-P-}C_5H_4PPh_2)_2(\mu\text{-Cl})M(CO)_3]$[18a] (M = Mo, W). The ^{31}P NMR spectrum at room temperature of this compound consists of one singlet signal at −3.5 ppm [$J(^{31}P-^{183}W)$ 216 Hz], thus indicating the coordination of the $W(CO)_3$ moiety to the PPh_2 group. The ^1H NMR spectrum at the same temperature displays multiplet signals at 5.69 and 5.50, and triplets at 5.63 and 4.83 ppm assigned to $C_5H_4PPh_2$ and $C_5H_4SiMe_3$ protons, respectively. Resonances attributable to the phenyl and $SiMe_3$ protons are also present. The ^{31}P and ^1H NMR spectra recorded at low temperatures show the existence of two isomers in solution (see Experimetal Section). The main features of the ^{31}P and ^1H NMR spectra, as well as the IR carbonyl pattern, for complex **4** are similar to those previously discuted for compound **3**.

By contrast with the research carried out on diphenylphosphinocyclopentadienyl ligand in different transition-metal systems, few studies have been performed with oxo- and thiophosphorylcyclopentadienyl groups. We have, therefore, considered it particularly interesting to explore the coordination chemisty of complexes $[(\eta^5\text{-}C_5H_4P(E)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (E = O,S), which have recently been prepared by us,[5] as an extension of the work previously presented for the complex $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$.

$[Mo(CO)_4(nbd)]$ was treated with $[(\eta^5\text{-}C_5H_4P(E)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (E = O,S) in toluene at room temperature and the reaction was followed by IR and ^1H NMR. Initially, after 30 min of stirring, compound $[(\eta^5\text{-}C_5H_4P(E)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-SPh})_2Mo(CO)_4]$ [E = S (**5**), O (**7**)] was detected as the major product together with traces of $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5\text{:}\kappa\text{-E-}C_5H_4P(E)Ph_2)(\mu\text{-SPh})_2Mo(CO)_3]$ [E = S (**6**), O (**8**)] and starting material. A few hours later complex **6** or **8** became the main product. All attempts to separate both type of compounds by chromatography or crystallization proved to be unsuccessful. Finally, after 15 h of reaction, the tricarbonyl derivatives were the sole species observed in solution. This result is evidence of the instability of tetracarbonyl species **5** and **7** through decarbonylation at room temperature, and it is in contrast with the behavior mentioned before for compounds **1** and **2**. Steric factors related to the proximity of O or S atom of the phosphorylcyclopentadienyl ligand to the molybdenum center could account for the higher stabilization of the tridentate coordination mode.

The IR spectra of complexes **5** and **7** in toluene present four bands attributable to a cis-disubstituted molybdenum tetracarbonyl complex. Further information concerning the chelation mode is obtained from their $^{31}P\{^1H\}$ NMR spectra at room temperature. Singlet resonances at 35.9 (**5**) and 21.0 ppm (**7**), hardly shifted with respect to the starting materials,[5] reveal the presence of uncoordinated oxo- or thiophosphoryl groups. The former data support the formulation of compounds **5** and **7** as titanium−molybdenum heterobimetallic complexes with double thiolato bridges.

The reaction of $[(\eta^5\text{-}C_5H_4P(E)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ (E = O,S) and $[Mo(CO)_3(NCMe)_3]$ proved to be a more convenient method to obtain derivatives **6** and **8** in high yield as violet crystalline solids. Both compounds are soluble in toluene, thf, and dichloromethane, and these solutions are quite stable.

They have been identified by both spectroscopic and elemental analyses. Their ν(CO) IR pattern in solution revealed the presence of *fac*-$Mo(CO)_3$ moieties. The IR solid spectra show bands at 634 (**6**) and 1144 cm^{-1} (**8**) assigned to the P = E (E = S, O) streching mode. The lowering in these stretching frequencies is consistent with a slight lengthening of the P = E bonds upon complexation of the molybdenum atom. The $^{31}P\{^1H\}$ NMR spectra at room temperature show a single phosphorus resonance, downfield shifted by 9.1 and 15.3 ppm with respect to the corresponding precursors. All these data clearly indicate a *fac*-E,S,S-$Mo(CO)_3$ (E = S, O) coordination mode in these heterobinuclear complexes.

Finally, reactions between $[(\eta^5\text{-}C_5H_4P(S)Ph_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$ and tungsten carbonyl fragments were also investigated. The reaction carried out under several conditions using $[W(CO)_4(nbd)]$ as a reagent did not allow us to obtain any satisfactory result. By contrast, the reaction with $[W(CO)_3(NCMe)_3]$ yielded almost inmediately the new heterobinuclear complex $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}S\text{-}C_5H_4P(S)Ph_2)(\mu\text{-}SPh)_2W(CO)_3]$ (**9**). Analytical and spectroscopic data for compound **9** are consistent with its formulation as a dinuclear Ti−W complex with S,S,S bridges. The ^1H and ^{31}P NMR spectra at low temperatures indicate the presence of one isomer in solution.

Crystal Structure of $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SPh)_2W(CO)_3]$ (3). Suitable crystals for the X-ray diffraction study were obtained by the slow diffusion of methanol into a dichloromethane solution of complex **3** at room temperature. An ORTEP drawing of the molecule is shown in Figure 2. Selected bond lengths and angles are given in Table 2.

Titanium atom in $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SPh)_2W(CO)_3]$ shows a pseudotetrahedral coordination sphere with angles Cp(1)−Ti−Cp(2) and S(1)−Ti−S(2) of 133.09 and 100.32°, respectively. Although there are no data on the crystalline structure of complex $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4SiMe_3)Ti(SPh)_2]$, the former angles as well as the Ti−S [2.474(4) and 2.513(4) Å] and Ti−Cp [2.047 and 2.095 Å] bond distances are in the range reported for other thiolate derivatives of titanocene $[Cp_2Ti(SPh)_2]$,[20] $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC_6F_5)_2]$,[21] and $[Cp_2Ti(SMe)_2]$.[22]

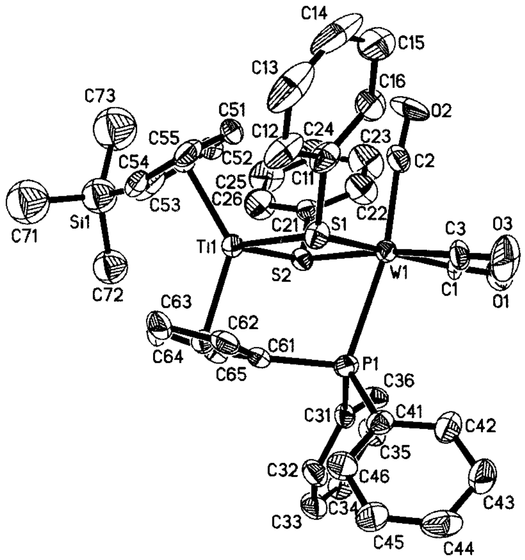


Figure 2. ORTEP drawing of compound **3**. Thermal ellipsoids are shown at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **3**[a]

	Bond Lengths		
Ti(1)−W(1)	3.206(3)	W(1)−C(1)	1.944(14)
Ti(1)−S(1)	2.474(4)	W(1)−C(2)	2.01(2)
Ti(1)−S(2)	2.513(4)	W(1)−C(3)	1.971(13)
W(1)−S(1)	2.493(3)	Ti(1)−Cp(1)	2.047
W(1)−S(2)	2.509(3)	Ti(1)−Cp(2)	2.095
W(1)−P(1)	2.543(3)		
	Bond Angles		
Cp(1)−Ti−Cp(2)	133.09	C(11)−S(1)−W(1)	118.7(6)
S(1)−Ti(1)−S(2)	100.32(13)	C(21)−S(2)−W(1)	117.5(4)
S(1)−W(1)−S(2)	99.92(11)	C(11)−S(1)−Ti(1)	120.1(5)
S(1)−W(1)−P(1)	81.74(11)	C(21)−S(2)−Ti(1)	118.7(5)
S(1)−W(1)−P(1)	76.33(10)	Ti(1)−S(1)−W(1)	80.40(11)
C(3)−W(1)−C(1)	81.4(6)	Ti(1)−S(2)−W(1)	79.35(12)
C(3)−W(1)−C(2)	94.7(6)		

[a] Cp(1) refers to the centroid of the ring formed by C51,C52,C53,C54,C55. Cp(2) refers to the centroid of the ring formed by C61,C62,C63,C64,C65.

The tungsten atom is octahedrally coordinated showing three carbonyl ligands in a facial arrangement with a P,S,S bridge between both metals. The W−S [2.509(3) and 2.493(3) Å], W−P [2.543(3) Å], and W−C [1.944(14), 2.01(2), and 1.971(13) Å] bond distances compare well with the $[\{W(CO)_3\}_2\{\mu\text{-}P(C_6H_4SMe\text{-}2)_2CH_2CH_2P(C_6H_4SMe\text{-}2)_2\}]$ carbonyl metal complex which exhibits a *fac*-P,S,S coordination mode.[19a]

The dihedral angle between S(1)−Ti−S(2) and S(1)−W−S(2) planes of 1.3° suggests that the TiS_2W central core is almost planar. This value is similar to those observed in other binuclear Ti(IV)−M complexes $[Cp_2Ti\{\mu\text{-}S(CH_2)_nPPh_2\}_2M]BF_4$ (n = 2, M = Cu; n = 3, M = Rh)[23] or $[Cp_2Ti(\mu\text{-}SMe)_2Mo(CO)_4]$[24] and is in contrast with TiS_2Cu puckered cores found in $[Cp_2Ti(\mu\text{-}SEt)_2CuL]$ (L = PPh_3, 13.2°; L = PCy_3, 17.92°)[25] or $[Cp_2Ti(\mu\text{-}SMe)_2Cu(NCMe)_2]PF_6$ (11°).[26]

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All mononuclear thiolate derivatives of titanocene which crystal structures have been solved, display the organic groups of the thiolate ligands in opposite sides of the S(1)−Ti−S(2) plane in an endo(anti) conformation. Heteronuclear species derived from these precursors have showed a preferential endo-(syn) conformation with the two groups located on the same side of the TiS_2M (M = Mo, W) plane. However, an X-ray diffraction study has been reported on the endo(anti) conformation of compound $[Cp_2Ti(\mu\text{-S-}p\text{-}C_6H_4Cl)_2Mo(CO)_4]$.[17] As we can see in Figure 2, complex **3** exhibits the two phenyl groups of the thiolate ligands orientated to the same side of the plane as corresponding to an endo(syn) conformer. The Ti−W bond distance of 3.206(3) Å is significantly larger than the sum of the covalent radii (2.66 Å).

Compound $[(\eta^5\text{-}C_5H_4SiMe_3)Ti(\mu\text{-}\eta^5{:}\kappa\text{-P-}C_5H_4PPh_2)(\mu\text{-SPh})_2W(CO)_3]$ (**3**) is the first heteronuclear species of a group 4 metallocene acting as tridentate ligand for which the crystal structure has been determined by X-ray diffraction.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of complex **3** is available on the Internet only. Access information is given on any current masthead page.

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