A Novel Organometallic Phosphine Ligand Containing Titanium(II), (η^5-C$_5$H$_5$)Ti(η^7-C$_7$H$_6$PPh$_2$), and Related Heterobimetallic Complexes: X-ray Structure of (η^5-C$_5$H$_5$)Ti(η^7-C$_7$H$_6$PPh$_2$)Mo(CO)$_5$·C$_6$H$_5$CH$_3$

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Addition of butyllithium to Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$) and subsequent reaction with Ph$_2$PCl afforded the titanium(II) phosphine Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_6$PPh$_2$) (3). Complex 3 shows coordinating capabilities, and by displacement of one carbonyl of Ni(CO)$_4$, Fe(CO)$_5$, and Mo(CO)$_6$ bimetallic complexes Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_6$PPh$_2$M(CO)$_n$) (5–7) were isolated in which the oxidation state (II) for titanium is retained. Infrared data indicated that phosphine 3 has a donating capability only slightly stronger than that of PPh$_3$. The compound Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_6$PPh$_2$Mo(CO)$_5$)·C$_6$H$_5$CH$_3$ crystallizes in the centrosymmetric group $P\bar{1}$ with cell dimensions a = 10.274 (4) Å, b = 14.228 (4) Å, c = 13.245 (4) Å, α = 111.71 (3)°, β = 67.84 (3)°, γ = 110.06 (3)°, and Z = 2. Refinement based on 3177 observed diffractometer data converged at R_w = 0.040. The molybdenum atom is roughly in the C$_7$-ring plane at a nonbonding distance of 5.442 (2) Å from the titanium atom, but the Mo–P–C(C$_7$H$_6$) angle (120.1 (3)°) is much larger than the Mo–P–C(C$_6$H$_5$) angles. The Ph$_2$PMo(CO)$_5$ group leads to the shortening of the Ti–C$_5$-ring distance (2.305 Å) and to the lengthening of the Ti–C$_7$-ring distance (2.203 Å); both planes are no longer parallel in the sandwich unit. The coordination of the molybdenum corresponds to an octahedron with a long Mo–P bond length (2.563 (2) Å) and a short trans-Mo–C(5) bond distance (1.960 (8) Å).

Introduction

In spite of increasing interest in heterobimetallic systems,[2] few of them containing a group 4A metal and involving a metal–metal bond such as Cp$_2$Ti–Mo(CO)$_3$Cp[3] or Cp$_2$-(CH$_3$)Zr–Mo(CO)$_3$Cp[4] have been reported. However, examples of heterobimetallic complexes where a group 4A metal is linked to another metal through bridging atoms such as oxygen, sulfur, or phosphorus,[2,5] bridging carbonyl groups,[6] or a bridging cyclopentadienyl ligand[7] are already known but they usually involve a high oxidation state (IV) and show a low reactivity.

In order to associate a group 4A metal in a low oxidation state to a second metal, bridging ligands having two independent coordination sites have to be elaborated. A promising field consists of the synthesis of bridging ligands containing a hydrocarbon cycle which coordinates to the 4A metal to give a stable bond. A first approach has been reported by the synthesis of the [(C$_6$H$_5$)$_2$PCH$_2$Si(CH$_3$)$_2$C$_5$H$_4$]$^-$ ligand, followed by its coordination to a Zr(IV) atom.[8]

In this direction we have orientated our efforts in the synthesis of heterobinuclear complexes including a titanium(II) atom, for which reduction properties resulting from the low oxidation state (II) could be expected.[5]

We report here (i) the preparation of a novel organometallic phosphine containing a titanium(II) atom, [Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_6$PPh$_2$)], starting from the sandwich complex Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$),[9] (ii) the access to heterobimetallic systems, for which the oxidation state II is retained for the

titanium, by coordination of the phosphorus group to metal carbonyls, and (iii) the X-ray diffraction structure of (η^5-C$_5$H$_5$)Ti(η^7-C$_7$H$_6$PPh$_2$)Mo(CO)$_5$·C$_6$H$_5$CH$_3$ in order to study the conformation of the molecule with respect to both metals and how the coordination of the phosphorus atom to molybdenum(0) modifies the sandwich unit.

Experimental Section

Synthesis. All reactions were carried out under argon atmosphere in dry, deoxygenated solvents. Chlorodiphenylphosphine (Alfa Inorganics) was distilled before use. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer.

Preparations. Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$) (1). Its preparation was based on one reported procedure,[10] and the yields were significantly improved by adding a small amount of FeCl$_3$ as activator. In a 1-L flask containing 20 g of magnesium chips were added 2 g of anhydrous FeCl$_3$, 50 mL of cycloheptatriene, 50 mL of THF, and, over a 3-h period to allow the warming of the stirred reaction mixture, a solution of 60 g (0.27 mol) of TiCl$_3$(C$_5$H$_5$) in 450 mL of THF. The mixture was stirred at room temperature for 12 h, and the volatile products were evaporated under vacuum. Sublimation of the residue (130 °C, 10^{-2} mmHg) gave a blue solid, which was washed with hexane and dried under vacuum: 88% yield (48.8 g); ^{1}H NMR (C$_6$D$_6$) δ 5.47 (s, C$_7$H$_7$), 4.97 (s, C$_5$H$_5$).[9]

Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_6$PPh$_2$) (3). A 12-mL quantity of a hexane solution of *n*-butyllithium (1.6 M) was added to a blue suspension, maintained at 0 °C, of 3.7 g (18.1 mmol) of 1 in 120 mL of ether. The mixture was stirred for 5 h at 0 °C to afford a black-green mixture containing 2 (an intermediate). Four grams (18.1 mmol) of PPh$_2$Cl was then added, and the stirring was maintained overnight. The solvents were removed under vacuum, and the residue was extracted with 120 mL of hot toluene. The cooling of the solution led to the formation of blue crystals of the phosphine 3. Filtration gave 4.8 g (68%) of the product. Anal. Calcd for C$_{24}$H$_{21}$PTi: C, 74.24; H, 5.45; P, 7.98. Found: C, 74.30; H, 5.73; P, 7.74. ^{1}H NMR (C$_6$D$_6$): δ 7.25 (m, C$_6$H$_5$); 6.05 (m, 2 H) and 5.60 (m, 4 H) (C$_7$H$_6$); 5.10 (s, C$_5$H$_5$).

[Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_6$PPh$_2$CH$_3$)]I (4). A suspension of 1 equiv of compound 3 in diethyl ether with 2 equiv of methyl iodide was stirred at room temperature for 2 days. Filtration gave in quantitative yield the blue salt 4. Although compound 4 slowly decomposes in acetonitrile solutions, crystals of 4 were obtained by fast crystallization in acetonitrile. Anal. Calcd for C$_{25}$H$_{24}$IPTi: C, 56.63; H, 4.56; P, 5.84; I, 23.93. Found: C, 56.11; H, 4.62; P, 5.38; I, 23.26.

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Table I. Relevant Crystallographic Data

compd	$Ti(\eta^5\text{-}C_5H_5)[\eta^7\text{-}C_7H_6PPh_2Mo(CO)_5]\cdot$ $C_6H_5CH_3$
formula	$TiMoPO_5C_{36}H_{29}$
mol wt	715.8
a	10.274 (4) Å
b	14.228 (4) Å
c	13.245 (4) Å
α	111.71 (3)°
β	67.84 (3)°
γ	110.06 (3)°
V	1619 Å³
Z	2
$F(000)$	728
t	20 °C
calcd density	1.467 g cm⁻³
measd density	1.45 ± 0.03 g cm⁻³
abs coeff	0.75 mm⁻¹
cryst syst	triclinic
space group	$P\bar{1}$
cryst size	(0.2 × 0.2 × 0.2) mm
radiation	Mo Kα (0.710 69 Å)
monochromator	graphite
cryst–counter dist	173 mm
scan angle	$(1.00 + 0.35 \tan \theta)°$
max scan time	120 s
receiving aperture	$2.00 + 0.35 \tan \theta$
no. of data collected	8900
no. of obsd data	3177
no. of refined variables	484
$R_w = \Sigma w[(|F_o| - |F_c|)^2/$ $\Sigma w |F_o|^2]^{1/2}$	0.040

$Ti(\eta^5\text{-}C_5H_5)[\eta^7\text{-}C_7H_6PPh_2Ni(CO)_3]$ (**5**). To a solution of 1.53 g (3.94 mmol) of phosphine **3** in 70 mL of hexane was added 2 g (11.7 mmol) of $Ni(CO)_4$. The solution was stirred at room temperature for 24 h and then concentrated and cooled at −20 °C. A yield of 1.3 g (62%) of blue crystals of **5** was then obtained by filtration. Anal. Calcd for $C_{27}H_{21}PO_3NiTi$: C, 61.07; H, 3.99; P, 5.83. Found: C, 60.87; H, 4.00; P, 5.71. IR (hexane): ν_{CO} 2067, 2005, and 1990 cm⁻¹. ^1H NMR (C_6D_6): δ 7.28 (m, C_6H_5); 6.38 (m, 4 H) and 5.65 (m, 2 H) (C_7H_6); 4.94 (s, C_5H_5).

$Ti(\eta^5\text{-}C_5H_5)[\eta^7\text{-}C_7H_6PPh_2Fe(CO)_4]$ (**6**). The mixture containing 5 g (12.9 mmol) of the phosphine **3**, 3.9 g (20 mmol) of $Fe(CO)_5$ and 70 mL of toluene was heated in an autoclave at 140 °C for 30 h. After cooling, the mixture was chromatographed on a neutral alumina column (toluene eluent). The blue fraction was recovered and gave blue crystals of **6** when the toluene was removed under vacuum; yield 2 g (28%). Anal. Calcd for $C_{28}H_{21}O_4PFeTi$: C, 60.47; H, 3.81; P, 5.57. Found: C, 60.33; H, 3.67; P, 5.43. IR (hexane): ν_{CO} 2049, 1981, 1952, and 1935 cm⁻¹. ^1H NMR (C_6H_6): δ 7.28 (m, C_6H_5); 6.50 (m, 2 H) and 5.53 (m, 4 H) (C_7H_6); 4.95 (s, C_5H_5).

$Ti(\eta^5\text{-}C_5H_5)[\eta^7\text{-}C_7H_6PPh_2Mo(CO)_5]\cdot C_6H_5CH_3$ (**7**). A solution of 2.7 g (6.96 mmol) of phosphine **3** and 1.9 g (7.2 mmol) of $Mo(CO)_6$ in 100 mL of toluene was refluxed for 2 h and then filtered, concentrated under vacuum, and cooled at −20 °C. The blue crystals of **7** that separated were washed with toluene and dried under vacuum; yield 3 g (60%). The slow cooling of a toluene solution of complex **7** afforded crystals suitable for X-ray analysis. Anal. Calcd for $C_{36}H_{29}O_5PMoTi$: C, 60.35; H, 4.08; P, 4.32. Found: C, 59.54; H, 4.11; P, 4.30. IR (Nujol): ν_{CO} 2080, 1995, 1940, and 1915 cm⁻¹.

Collection and Reduction of X-ray Data. Crystals of the title complex $Ti(\eta^5\text{-}C_5H_5)[(\eta^7\text{-}C_7H_6)PPh_2Mo(CO)_5]\cdot C_6H_5CH_3$ suitable for X-ray analysis were obtained by crystallization in toluene. A crystal of approximate dimensions of 0.2 mm was mounted in a sealed Lindemann tube under an inert atmosphere. Preliminary photographic data showed that the crystal belonged to the triclinic system. Accurate cell parameters were obtained by a least-squares analysis of 25 carefully centered diffractometer reflections from diverse regions of reciprocal space. Table I gives the pertinent crystal data and all the details of data collection intensities, which were collected with use of the $\omega/2\theta$ method on a Nonius CAD-4 automated diffractometer using Mo Kα radiation (λ = 0.710 69 Å). All the 3177 independent reflections measured having $I > 2.5\sigma(I)$ were used in the structure solution and refinement. The data were corrected for Lorentz-polarization effects. No correction for absorption was deemed necessary because of the small size of the crystal and the very small linear absorption coefficient

Scheme I
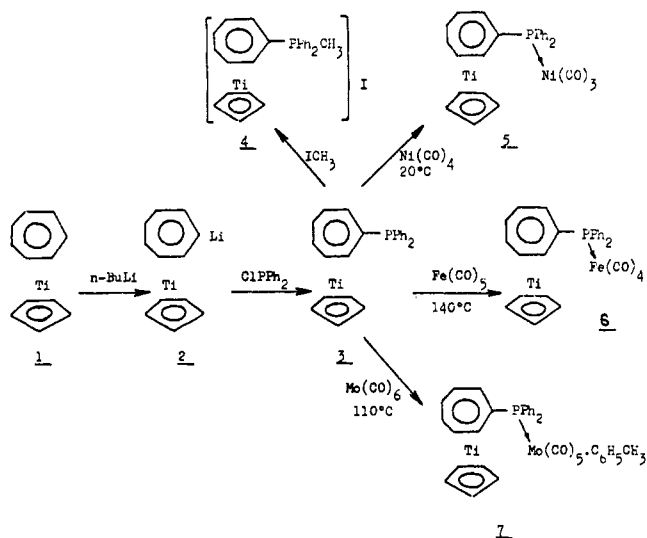
($\mu = 0.75$ mm⁻¹). The two standard reflections monitored every hour of exposure did not show any significant changes in intensity throughout the course of data collection.

Solution and Refinement of the Structure. All calculations were performed on a IRIS 50 computer. Atomic scattering factors were taken from a tabulation by Cromer and Mann. The positions of the heaviest atoms (Mo, Ti, P) were found with the aid of the SHELX[11] program from the examination of the Patterson function, of the centrosymmetric $P\bar{1}$ space group. The positions of all the remaining non-hydrogen atoms were located from a three-dimensional electron density difference map. Refinement of the scale factor and positional and isotropic thermal parameters of these 44 atoms by a full-matrix least-squares technique led to an R value of 0.072. After anisotropic refinement of all these atoms ($R = 0.055$), a Fourier difference map showed the positions of all the independent hydrogen atoms. With isotropic thermal parameters fixed at 5.0 Å², the hydrogen atom coordinates were refined along with the non-hydrogen anisotropic parameters to give a convergence for $R = 0.042$ and $R_w = 0.040$. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, with the weighting scheme $w^{1/2} = 1$ if $F_o < P_1$ and $w^{1/2} = P_1/F_o$ if $F_o > P_1$ with $P_1 = (F_o(\text{max})^2/10)^{1/2}$ and with the aid of CRISAFFI, a program by Marsau.[12] The maximum shift/esd of the last cycle was 0.2, and the final difference was devoid of any significant features. Table II lists the atomic parameters of atoms with their esd's. The most significant bond distances and angles are given in Tables III and IV, respectively.

Results and Discussion

Synthetic Aspects. It had been shown[13] that the lithiation of the titanium(II) complex $Ti(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$ (**1**),[9] performed by treatment with *n*-butyllithium in ether, occurred essentially (95%) at the seven-membered ring. Solutions containing the intermediate **2** could then be used to selectively introduce a functional group on the cycloheptatrienyl ligand. Thus the treatment of an ether solution of **2** at 0 °C with 1 equiv of chlorodiphenylphosphine led us to the isolation of the blue titanium(II)-containing phosphine **3** with 68% yield (Scheme I).[14]

The novel phosphine **3** is stable under inert atmosphere and reacts slowly with an excess of methyl iodide to afford quantitatively the phosphonium salt **4**. This reaction indicates that the 16-electron complex **3** is rather stable to the oxidative addition of the titanium(II) by alkyl halides and that the

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.1966 (1)	0.0313 (0)	0.2070 (1)	0.0091 (1)	0.0039 (0)	0.0055 (0)	0.0015 (0)	−0.0023 (0)	0.0009 (0)
Ti(1)	0.0319 (1)	0.3462 (1)	0.1843 (1)	0.0104 (2)	0.0046 (1)	0.0046 (1)	0.0020 (1)	−0.0029 (1)	0.0013 (1)
P(1)	0.1930 (2)	0.2235 (1)	0.3050 (1)	0.0068 (2)	0.0030 (1)	0.0038 (1)	0.0009 (1)	−0.0019 (1)	0.0007 (1)
C(1)	0.1882 (8)	0.0369 (5)	0.0587 (6)	0.0123 (11)	0.0047 (5)	0.0070 (6)	0.0018 (6)	−0.0035 (7)	0.0003 (4)
O(1)	0.1792 (7)	0.0360 (5)	−0.0240 (5)	0.0221 (11)	0.0106 (5)	0.0076 (5)	0.0041 (6)	−0.0045 (6)	0.0019 (4)
C(2)	0.4152 (8)	0.0714 (5)	0.1569 (6)	0.0101 (10)	0.0047 (5)	0.0084 (7)	0.0019 (5)	−0.0030 (7)	0.0012 (4)
O(2)	0.5383 (6)	0.0903 (5)	0.1280 (6)	0.0096 (8)	0.0094 (5)	0.0161 (8)	0.0019 (5)	−0.0028 (6)	0.0037 (5)
C(4)	−0.0248 (8)	−0.0173 (6)	0.2586 (7)	0.0112 (11)	0.0060 (5)	0.0092 (7)	0.0020 (6)	−0.0028 (7)	0.0030 (5)
O(4)	−0.1457 (6)	−0.0458 (5)	0.2888 (6)	0.0105 (8)	0.0112 (6)	0.0188 (9)	0.0011 (6)	−0.0028 (7)	0.0083 (6)
C(3)	0.1936 (9)	0.0130 (5)	0.3552 (6)	0.0178 (13)	0.0043 (5)	0.0073 (7)	0.0026 (6)	−0.0043 (8)	0.0008 (4)
O(3)	0.1886 (9)	−0.0022 (5)	0.4346 (5)	0.0362 (16)	0.0084 (5)	0.0100 (6)	0.0042 (7)	−0.0089 (8)	0.0030 (5)
C(5)	0.2134 (8)	−0.1134 (5)	0.1359 (7)	0.0127 (11)	0.0042 (4)	0.0087 (7)	0.0020 (6)	−0.0041 (7)	0.0004 (4)
O(5)	0.2262 (7)	−0.1981 (4)	0.0944 (5)	0.0197 (10)	0.0048 (4)	0.0138 (7)	0.0039 (5)	−0.0049 (7)	−0.0000 (4)
C(11)	0.0397 (11)	0.3857 (8)	0.0294 (7)	0.0201 (16)	0.0148 (10)	0.0077 (8)	0.0065 (10)	−0.0027 (9)	0.0066 (7)
C(12)	0.1391 (12)	0.4663 (7)	0.0807 (8)	0.0274 (19)	0.0066 (6)	0.0094 (8)	0.0041 (9)	0.0005 (10)	0.0051 (6)
C(13)	0.2470 (9)	0.4199 (7)	0.0715 (7)	0.0124 (12)	0.0107 (8)	0.0078 (7)	0.0009 (8)	−0.0015 (7)	0.0052 (6)
C(14)	0.2142 (10)	0.3179 (7)	0.0140 (7)	0.0171 (15)	0.0109 (8)	0.0072 (7)	0.0061 (9)	0.0001 (8)	0.0031 (6)
C(15)	0.0912 (11)	0.2976 (7)	−0.0107 (7)	0.0244 (18)	0.0101 (8)	0.0056 (7)	0.0042 (9)	−0.0046 (9)	0.0019 (6)
C(21)	0.0582 (7)	0.2766 (4)	0.2980 (5)	0.0079 (8)	0.0037 (4)	0.0041 (5)	0.0017 (4)	−0.0020 (5)	0.0012 (3)
C(22)	−0.0463 (7)	0.2047 (5)	0.2424 (6)	0.0091 (9)	0.0038 (4)	0.0064 (6)	0.0011 (5)	−0.0034 (6)	0.0011 (4)
C(23)	−0.1616 (8)	0.2288 (6)	0.2249 (7)	0.0109 (10)	0.0056 (5)	0.0097 (7)	0.0016 (6)	−0.0055 (7)	0.0019 (5)
C(24)	−0.2043 (8)	0.3163 (6)	0.2593 (7)	0.0099 (10)	0.0075 (6)	0.0096 (8)	0.0020 (6)	−0.0046 (7)	0.0032 (5)
C(25)	−0.1423 (9)	0.4156 (6)	0.3188 (6)	0.0139 (12)	0.0060 (5)	0.0074 (7)	0.0048 (6)	−0.0027 (7)	0.0016 (5)
C(26)	−0.0212 (8)	0.4465 (5)	0.3592 (6)	0.0132 (11)	0.0045 (4)	0.0054 (5)	0.0031 (6)	−0.0023 (6)	0.0004 (4)
C(27)	0.0685 (7)	0.3851 (5)	0.3496 (5)	0.0106 (9)	0.0041 (4)	0.0037 (5)	0.0020 (5)	−0.0023 (5)	0.0006 (3)
C(31)	0.1573 (7)	0.2502 (4)	0.4579 (5)	0.0094 (9)	0.0024 (3)	0.0043 (5)	0.0009 (4)	−0.0025 (5)	0.0006 (3)
C(32)	0.2619 (8)	0.2499 (5)	0.5004 (6)	0.0123 (10)	0.0042 (4)	0.0066 (6)	0.0008 (5)	−0.0050 (6)	0.0014 (4)
C(33)	0.2313 (9)	0.2616 (5)	0.6168 (7)	0.0183 (13)	0.0047 (5)	0.0085 (7)	−0.0001 (6)	−0.0085 (8)	0.0021 (5)
C(34)	0.1003 (10)	0.2731 (6)	0.6857 (6)	0.0219 (15)	0.0056 (5)	0.0048 (6)	0.0017 (7)	−0.0045 (8)	0.0010 (4)
C(35)	−0.0063 (9)	0.2715 (6)	0.6464 (6)	0.0157 (12)	0.0063 (5)	0.0050 (6)	0.0032 (6)	−0.0011 (7)	0.0020 (4)
C(36)	0.0212 (8)	0.2598 (5)	0.5322 (6)	0.0118 (10)	0.0049 (4)	0.0048 (5)	0.0019 (5)	−0.0019 (6)	0.0016 (4)
C(41)	0.3641 (7)	0.3181 (5)	0.2662 (5)	0.0074 (8)	0.0041 (4)	0.0055 (5)	0.0016 (5)	−0.0025 (5)	0.0018 (4)
C(42)	0.4429 (8)	0.3030 (5)	0.1526 (6)	0.0103 (10)	0.0048 (4)	0.0064 (6)	0.0016 (5)	−0.0023 (6)	0.0018 (4)
C(43)	0.5687 (8)	0.3742 (6)	0.1171 (7)	0.0098 (10)	0.0070 (5)	0.0078 (7)	0.0025 (6)	−0.0008 (6)	0.0036 (5)
C(44)	0.6145 (8)	0.4628 (6)	0.1950 (7)	0.0088 (10)	0.0068 (5)	0.0113 (8)	0.0003 (6)	−0.0026 (7)	0.0051 (6)
C(45)	0.5392 (9)	0.4787 (5)	0.3054 (7)	0.0121 (11)	0.0041 (5)	0.0118 (8)	0.0002 (6)	−0.0054 (8)	0.0017 (5)
C(46)	0.4138 (8)	0.4075 (5)	0.3444 (6)	0.0111 (10)	0.0045 (4)	0.0071 (6)	0.0010 (5)	−0.0036 (6)	0.0017 (4)
C(51)	0.4669 (11)	0.8183 (8)	0.2912 (9)	0.0163 (16)	0.0127 (9)	0.0167 (12)	0.0029 (10)	−0.0042 (11)	0.0078 (9)
C(52)	0.4309 (12)	0.7122 (9)	0.2415 (10)	0.0217 (19)	0.0124 (10)	0.0145 (12)	0.0031 (11)	−0.0064 (12)	0.0041 (9)
C(53)	0.3649 (13)	0.6539 (9)	0.3136 (10)	0.0238 (20)	0.0122 (10)	0.0156 (12)	0.0030 (11)	−0.0069 (13)	0.0044 (9)
C(54)	0.3347 (12)	0.6857 (9)	0.4268 (10)	0.0195 (18)	0.0122 (10)	0.0184 (14)	0.0026 (11)	−0.0050 (13)	0.0057 (9)
C(55)	0.3686 (13)	0.7833 (10)	0.4728 (10)	0.0242 (22)	0.0179 (13)	0.0157 (14)	0.0075 (14)	−0.0031 (14)	0.0046 (11)
C(56)	0.4322 (14)	0.8541 (9)	0.4070 (11)	0.0301 (23)	0.0099 (9)	0.0184 (14)	0.0039 (12)	−0.0094 (15)	0.0012 (9)
C(57)	0.5341 (14)	0.8838 (10)	0.2156 (12)	0.0254 (23)	0.0179 (13)	0.0212 (16)	0.0034 (14)	−0.0065 (16)	0.0085 (12)

	x	y	z		x	y	z
H(11)	−0.0381 (76)	0.3931 (54)	0.0293 (59)	H(36)	−0.0586 (76)	0.2518 (53)	0.5062 (59)
H(12)	0.1485 (76)	0.5254 (54)	0.1197 (59)	H(42)	0.4145 (76)	0.2417 (53)	0.1039 (59)
H(13)	0.3237 (76)	0.4540 (54)	0.0943 (60)	H(43)	0.6129 (76)	0.3589 (54)	0.0400 (59)
H(14)	0.2727 (76)	0.2754 (53)	−0.0012 (59)	H(44)	0.6840 (78)	0.5077 (53)	0.1779 (59)
H(15)	0.0497 (76)	0.2301 (54)	−0.0465 (59)	H(45)	0.5644 (76)	0.5258 (53)	0.3473 (59)
H(22)	−0.0312 (75)	0.1425 (53)	0.2123 (59)	H(46)	0.3551 (76)	0.4188 (53)	0.4192 (59)
H(23)	−0.2141 (76)	0.1647 (53)	0.1740 (59)	H(52)	0.4511 (76)	0.6812 (53)	0.1551 (59)
H(24)	−0.2719 (76)	0.3108 (53)	0.2298 (59)	H(53)	0.3406 (76)	0.5776 (53)	0.2760 (59)
H(25)	−0.1719 (77)	0.4629 (54)	0.3203 (59)	H(54)	0.2816 (77)	0.6311 (54)	0.4788 (59)
H(26)	0.0184 (76)	0.5135 (54)	0.3904 (60)	H(55)	0.3571 (76)	0.8137 (53)	0.5545 (59)
H(27)	0.1425 (76)	0.4227 (53)	0.3739 (59)	H(56)	0.4558 (76)	0.9325 (52)	0.4422 (58)
H(32)	0.3299 (76)	0.2361 (53)	0.4609 (59)	H(57)	0.4871 (76)	0.9526 (53)	0.2913 (59)
H(33)	0.3038 (76)	0.2550 (53)	0.6275 (59)	H(58)	0.5089 (76)	0.8148 (53)	0.1389 (59)
H(34)	0.0794 (75)	0.2809 (53)	0.7617 (59)	H(59)	0.6511 (75)	0.9388 (53)	0.2320 (59)
H(35)	−0.1016 (76)	0.2775 (54)	0.6952 (60)				

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.
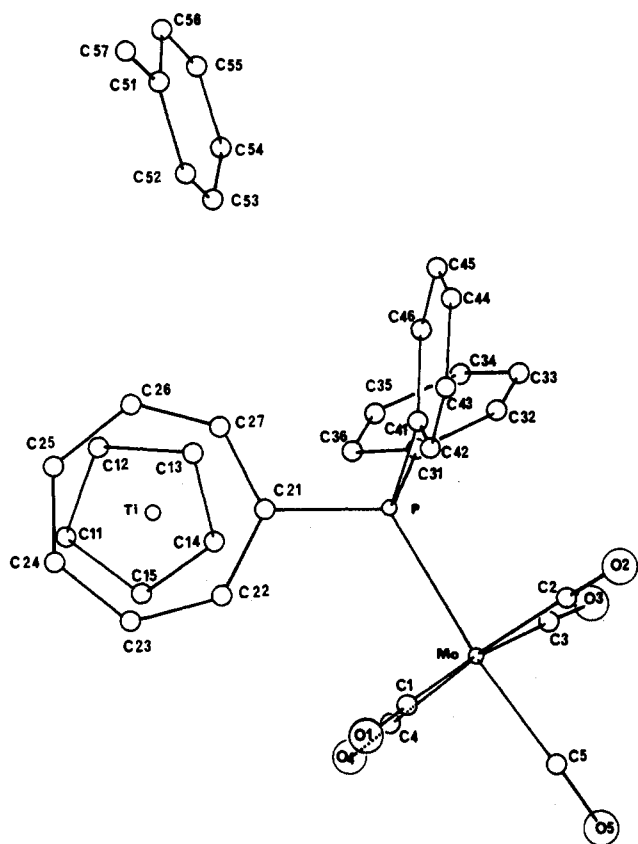
phosphorus atom keeps its nucleophilic character.

In addition, the phosphorus group of the organometallic phosphine 3 retains its coordinating capability and can be used for the formation of heterobimetallic complexes. One carbonyl of metal carbonyls such as $Ni(CO)_4$, $Fe(CO)_5$, or $Mo(CO)_6$ could be displaced, and coordination of the phosphine 3 took place. Thus on treatment of 3 with $Ni(CO)_4$ in hexane, at room temperature, the blue titanium(II)–nickel(0) complex 5 was formed and isolated in 62% yield (Scheme I). Phosphine 3 was reacted with neat $Fe(CO)_5$ in an autoclave at 140 °C, and 28% of derivative 6 was isolated with use of chromatog-

raphy. After 3 was refluxed with a slight excess of $Mo(CO)_6$ in toluene, the blue bimetallic complex 7, which has a very low solubility in toluene, crystallized in 68% yield. Derivatives 5–7 gave satisfactory elementary analyses.
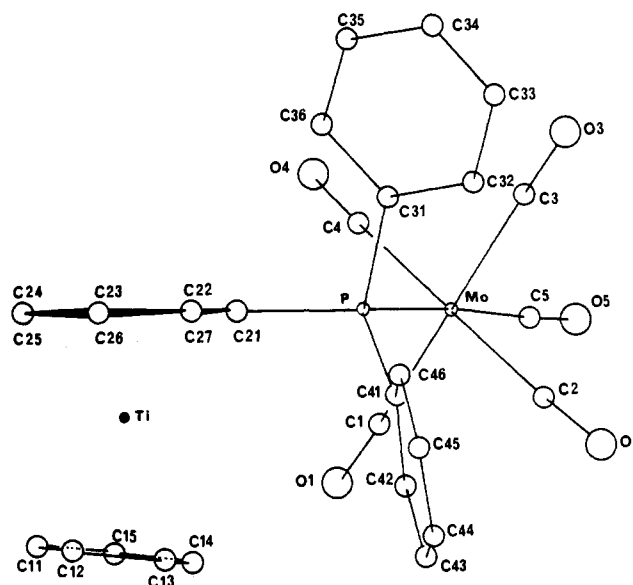
The complexes 5–7 showed in their infrared spectrum terminal carbonyls only, indicating the absence of titanium–metal interactions, which would have given subsequent bridging of one carbonyl. Therefore the titanium retains a d^2 configuration in these 16-electron titanium(II) complexes. The infrared data allows the comparison of the electronic effect of the phosphine 3 with that of other phosphorus ligands in the $Ni(CO)_3L$ series

Table III. Selected Bond Distances (Å) and Esd's

Ti–C(11)	2.287 (11)	C(11)–C(12)	1.401 (16)
Ti–C(12)	2.306 (12)	C(12)–C(13)	1.421 (15)
Ti–C(13)	2.301 (9)	C(13)–C(14)	1.356 (13)
Ti–C(14)	2.328 (10)	C(14)–C(15)	1.334 (15)
Ti–C(15)	2.302 (11)	C(15)–C(11)	1.373 (15)
Ti–C(21)	2.217 (7)	C(21)–C(22)	1.423 (10)
Ti–C(22)	2.205 (7)	C(22)–C(23)	1.408 (10)
Ti–C(23)	2.196 (8)	C(23)–C(24)	1.404 (11)
Ti–C(24)	2.201 (8)	C(24)–C(25)	1.400 (12)
Ti–C(25)	2.204 (9)	C(25)–C(26)	1.407 (10)
Ti–C(26)	2.199 (8)	C(26)–C(27)	1.418 (10)
Ti–C(27)	2.196 (7)	C(27)–C(21)	1.422 (10)
Mo–P	2.563 (2)	P–C(21)	1.834 (7)
Mo–C(1)	2.030 (8)	P–C(31)	1.829 (7)
Mo–C(2)	2.022 (8)	P–C(41)	1.836 (7)
Mo–C(3)	2.061 (9)		
Mo–C(4)	2.054 (8)	C(1)–O(1)	1.129 (10)
Mo–C(5)	1.960 (8)	C(2)–O(2)	1.138 (10)
		C(3)–O(3)	1.129 (12)
Mo···O(1)	3.157 (7)	C(4)–O(4)	1.126 (10)
Mo···O(2)	3.159 (6)	C(5)–O(5)	1.156 (10)
Mo···O(3)	3.189 (9)		
Mo···O(4)	3.179 (6)	P···Ti	3.793 (3)
Mo···O(5)	3.116 (7)	Ti···Mo	5.442 (2)

Figure 2. View of the molecule $Ti(\eta^5\text{-}C_5H_5)[(\eta^7\text{-}C_7H_6PPh_2)Mo(CO)_5] \cdot C_6H_5CH_3$ in the direction parallel to the C_7 ring plane.
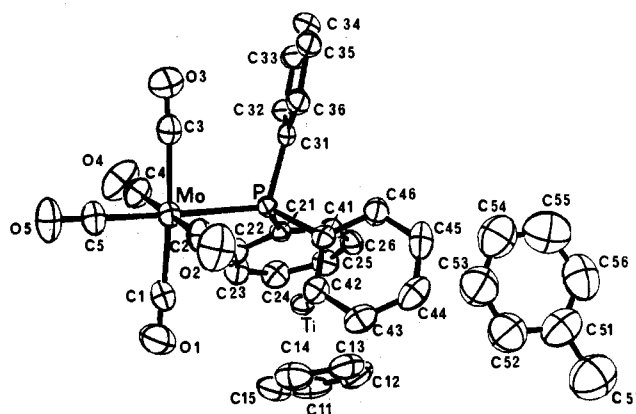
Figure 3. ORTEP drawing of $Ti(\eta^5\text{-}C_5H_5)[(\eta^7\text{-}C_7H_6PPh_2)Mo(CO)_5] \cdot C_6H_5CH_3$ with the atoms represented by their 50% probability ellipsoids for thermal motion.

Figure 1. Orthogonal projection on the C_7 ring plane of the molecule $Ti(\eta^5\text{-}C_5H_5)[(\eta^7\text{-}C_7H_6PPh_2)Mo(CO)_5] \cdot C_6H_5CH_3$.

studied by Tolman.[15] The $Ni(CO)_3P(OPh)_3$ complex was used as internal standard, and the comparison of **5** with $Ni(CO)_3PPh_3$ showed that the higher frequency carbonyl absorption band of **5** (2067 cm^{-1}) is actually lower by 2 ± 0.5 cm^{-1} than the corresponding band of $Ni(CO)_3PPh_3$ (2069 cm^{-1}). Therefore, the electronic effect of the phosphine **3** is not very different from the effect of PPh$_3$. The χ coefficient[15] of the group $(\eta^5\text{-}C_5H_5)Ti(\eta^7\text{-}C_7H_6)$ bonded to phosphorus is 2.3 ± 0.5 cm^{-1}, which is close to the value of $\chi = 2.6$ cm^{-1}

found for the methyl group as compared to $\chi = 4.3$ cm^{-1} for the phenyl group. Hence a donating capability of phosphine **3** slightly stronger than that of PPh$_3$ is expected.

The availability of crystals of **7** led us to determine its X-ray structure. Very few structural studies of titanium(II) complexes have been carried out, and those of $Ti(CO)_2(\eta^5\text{-}C_5H_5)_2$[16] and $Ti(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$[17] have been reported. Of special interest will be the direct comparison of structural data of the latter complex with those of **7**; thus we expect to observe the influence of the $-PPh_2Mo(CO)_5$ substituent on the sandwich unit. Morever, the structure of **7** is expected to give information on the relative position of the metal atoms.

Description and Discussion of the Molecular Structure of $Ti(\eta^5\text{-}C_5H_5)[\eta^7\text{-}C_7H_6PPh_2Mo(CO)_5]C_6H_5CH_3$ (7). Perspective views of the molecular geometry are illustrated in Figures 1 and 2 and show that the $Ti(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_6)$ moiety retains a sandwich structure. Figure 3 displays the thermal ellipsoids representing the atoms.

The values of the equivalent isotropic parameters B_{eq} of $(C_5H_5)C$ atoms are larger (4.76–5.61 Å^2) than those of the C_7H_6 ring (2.49–4.29 Å^2). The amplitude of the C thermal oscillations can be correlated to the strength of the Ti–ring

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Table IV. Selected Bond Angles (Deg) and Standard Deviations

P-Mo-C(1)	93.4 (4)	C(11)-C(12)-C(13)	105.8 (1.3)
P-Mo-C(2)	89.8 (4)	C(12)-C(13)-C(14)	108.1 (1.2)
P-Mo-C(3)	90.4 (4)	C(13)-C(14)-C(15)	108.7 (1.3)
P-Mo-C(4)	93.0 (4)	C(14)-C(15)-C(11)	110.6 (1.3)
P-Mo-C(5)	175.3 (6)	C(15)-C(11)-C(12)	106.8 (1.3)
Mo-C(1)-O(1)	177.0 (7)	C(21)-C(22)-C(23)	129.0 (0.9)
Mo-C(2)-O(2)	177.5 (7)	C(22)-C(23)-C(24)	128.9 (1.0)
Mo-C(3)-O(3)	176.5 (8)	C(23)-C(24)-C(25)	128.9 (1.0)
Mo-C(4)-O(4)	177.7 (7)	C(24)-C(25)-C(26)	128.5 (1.0)
Mo-C(5)-O(5)	178.5 (7)	C(25)-C(26)-C(27)	128.7 (0.9)
C(1)-Mo-C(2)	91.3 (6)	C(26)-C(27)-C(21)	129.0 (0.9)
C(1)-Mo-C(3)	175.1 (8)	C(27)-C(21)-C(22)	126.9 (0.9)
C(1)-Mo-C(4)	90.3 (6)	P-C(21)-C(22)	116.6 (6)
C(1)-Mo-C(5)	89.4 (6)	P-C(21)-C(27)	116.5 (6)
C(2)-Mo-C(3)	91.7 (6)	P-C(31)-C(32)	120.0 (6)
C(2)-Mo-C(4)	176.7 (8)	P-C(31)-C(36)	121.0 (6)
C(2)-Mo-C(5)	86.5 (6)	P-C(41)-C(42)	118.5 (6)
C(3)-Mo-C(4)	86.5 (6)	P-C(41)-C(46)	122.9 (6)
C(3)-Mo-C(5)	86.9 (6)	C(21)-P-C(31)	102.3 (6)
C(4)-Mo-C(5)	90.7 (6)	C(21)-P-C(41)	103.5 (6)
Mo-P-C(21)	120.1 (3)	C(31)-P-C(41)	103.0 (6)
Mo-P-C(31)	109.8 (3)		
Mo-P-C(41)	115.9 (3)		

bond; the stronger the Ti-C(ring) bond, the smaller the thermal parameter. Furthermore, the weaker agitation of $(C_7H_6)C$ atoms can also be explained by the additional link to the $PPh_2Mo(CO)_5$ group: the C(21) atom, which is bonded to the phosphorus atom, has a very small B_{eq} value (2.49 Å^2) whereas the other C atoms show an increasing of the thermal parameter with the distance from the P atom, the two farthest C atoms having the maximum values (4.12 and 4.29 Å^2).

Figure 2 shows that both the P-C(21) and the P-Mo bonds are roughly in the ring plane, the molybdenum atom being slightly shifted toward the titanium atom at 0.03 Å from the C_7H_6 ring plane. The Ti atom is at a 5.442 (2) Å distance from the Mo atom, so that no direct interaction between the metal atoms can be considered. The phenyl groups bonded to phosphorus are equivalently displaced on each side of the C_7H_6 ring plane, but they have different orientations as compared to the $Mo(CO)_5$ group probably due to the proximity on one side of the bulky $Ti(C_5H_5)$ group.

Figure 1 shows the molecule of toluene, which is away from the complex and has only a very weak interaction with it (C···H $\simeq$ 3.0-3.2 Å).

Ti(C$_5$H$_5$)(C$_7$H$_6$) Sandwich Moeity. Data for this group can be compared directly to those of the precursor Ti(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)[17] (1). Both rings are planar, but they are slightly away from being parallel (Table S1, supplementary material) whereas they are parallel in 1. The Ti atom is exactly at the section of the axes going through the center of gravity of each ring, and the axes make an angle of only 5.6 (2)°. It is noteworthy that the Ti-C(1i) distances are shorter in 7 (2.305 Å) than in 1 (2.321 Å) whereas the Ti···C(2i) distances are slightly longer in 7 (2.203 Å) than in 1 (2.194 Å). The Ti atom is much closer to the C_7H_6 ring (1.484 Å) than to the C_5H_5 ring (1.985 Å) as was already observed in 1 (1.490 and 1.994 Å, respectively[17]).

The surprisingly short Ti-C$_7$H$_7$-ring distance may be explained in terms of a strengthening of the corresponding bond by an electron transfer from the formal d^2 titanium(II) atom toward the C$_7$H$_7$ ligand. This electron redistribution would shift the formal (η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)Ti^{II} toward the canonical form (η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)Ti^{IV}, in which the C$_7$H$_7$ ligand would be considered as a formal triradical diene. This electron transfer is supported by the low reactivity of complexes 7 and 1 as compared to what would be expected for a 16-electron titanium(II) complex. However, complex 1 keeps a strong reducing property, for the treatment of complex 1 with an-

hydrous HCl in diethyl ether[18] gave quantitatively the known violet polymeric titanium(III) complex [CpTiCl$_2$]$_n$. Therefore, 1 and its derivatives are still best described as titanium(II) complexes.

Environment of the Phosphorus Atom. The environment of the phosphorus atom is tetrahedral. The P-C(21) is, as expected, in the 7-carbon-ring plane, but surprisingly the P-Mo bond is very close to this plane (Figure 2) so that the phenyl groups are almost equivalently displaced on each side of the C(21)-P-Mo plane [C(21)-P-C(31) = 102.3 (6)°, C(21)-P-C(41) = 103.5 (6)°, Mo-P-C(31) = 109.8 (3)°, Mo-P-C(41) = 115.9 (3)°]. The three C-P-C angles are equivalent [C(31)-P-C(41) = 103.0 (6)°]. The C-P-C angles are always shorter than the M-P-C angles, as it is observed, for instance, in Mo(CO)$_4$(Ph$_2$PCH$_2$PPh$_2$).[19] The dihedral angles of the phosphorus subsitutent planes are shown in Table S1. More distortion is found in the Mo-P-C angles [Mo-P-C(21) = 120.1 (3)°] as compared to that in Mo-P-C(C$_6$H$_5$) angles, and this is clearly due to the bulkiness of the Mo(CO)$_5$ unit in the plane of the C$_7$ ring. The P-C(21) bond length [1.834 (7) Å] is equivalent to P-C(31) [1.829 (7) Å] and to P-C(41) [1.836 (6) Å]. This implies that a strong effect of the coordinated C$_7$H$_6$ substituent as compared to the phenyl groups is not to be expected.

Coordination of Molybdenum. The coordination of the molybdenum corresponds to an almost regular octahedron with the phosphorus atom at one apical position and the P-Mo-C(5) angle of 175.3 (6)° (Figure 1). The molybdenum atom is shifted toward the phosphorus atom and is 0.05 Å above the equatorial atom plane, which is 0.08 Å above the equatorial oxygen atom plane in the same direction.

The four equatorial carbonyls are equivalent with average Mo-C bond distances of 2.04 Å and C-O bond lengths of 1.13 Å. The apical carbonyl shows a shorter Mo-C bond length [Mo-C(5) = 1.960 (8) Å] and a longer C-O bond length [C(5)-O(5) = 1.156 (10) Å]. This modification in the Mo-C-O linkage is consistent with the presence of an electron-donating group in the trans position to the carbonyl which increases the Mo-C π back-bonding such as in Mo(CO)$_4$-(Ph$_2$PCH$_2$PPh$_2$);[19] this modification was not observed for less electron-donating phosphorus groups such as in Mo(CO)$_5$PF$_3$[20] or Mo(CO)$_5$(P$_4$S$_3$).[21]

Finally the P-Mo bond length of 2.563 (2) Å can be compared to other phosphorus-molybdenum bond distances in phosphorus-group pentacarbonyl molybdenum(0) complexes such as Mo(CO)$_5$P[(CH$_2$)$_6$N$_3$][22] (2.479 Å) and Mo(CO)$_5$-(P$_4$S$_3$)[21] [2.471 (9) Å] or in the cis-disubstituted Mo(CO)$_4$-(Ph$_2$PCH$_2$PPh$_2$)[19] [2.535 (3) and 2.501 (2) Å]. This indicates a very long Mo-P bond length in 7. In addition the comparison of the P-Mo bond length in 7 to those found in the (μ-H)-[Mo(CO)$_4$PMePh$_2$]$_2^-$ anion[23] [2.541 (4) and 2.553 (4) Å] is of special interest, for we have shown by infrared data that the PMePh$_2$ ligand presents a donating capability very similar to that of the phosphine 3. Therefore the slightly longer P-Mo bond distance in the neutral complex 7 is not related to the electron-donor effect of the phosphine but may be related to the steric hindrance of the organometallic phosphine 3.

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Template Syntheses of 1,2-Alkene Dichalcogenide Chelates via the Addition of Activated Acetylenes to Dicyclopentadienyltitanium Pentachalcogenides
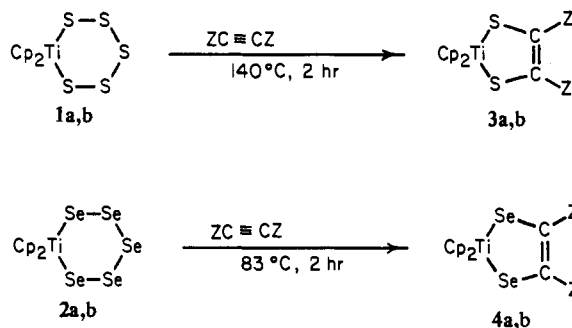
C. MARK BOLINGER and THOMAS B. RAUCHFUSS*

The pentachalcogenides $(C_5H_4R)_2TiE_5$ (R = H, CH_3; E = S, Se) react with acetylenes, $ZC\equiv CZ$ (Z = CO_2CH_3, CF_3) to give the alkene dichalcogenide compounds, $(C_5H_4R)_2TiE_2C_2Z_2$, which were isolated as dark green crystalline solids. The dithiolene syntheses proceed in ca. 40% yield at 140 °C while the corresponding diselenene synthesis was quantitative at 80 °C. The new compounds were characterized by ^1H, ^{13}C, ^{19}F, and ^{77}Se NMR, IR, mass spectrometry, and electrochemistry. $(C_5H_4CH_3)_2TiS_2C_2(CO_2CH_3)_2$ crystallizes in the triclinic space group $P\bar{1}$-C_i^1 (No. 2) with one molecule per unit cell of dimensions a = 9.312 (2) Å, b = 9.886 (2) Å, c = 11.225 (3) Å, α = 109.35 (2)°, β = 88.25 (2)°, and γ = 105.78 (2)°. Empirically weighted full-matrix least-squares refinement employing isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others converged to R_1(based on f) = 0.032 and R_2 = 0.039 for 4098 independent reflections having $2\theta_{MoK\alpha} \le 58.7°$ and $I > 3\sigma(I)$. The structure analysis revealed a conventional bis(methylcyclopentadienyl)titanium moiety chelated by the sulfur atoms of the dithiolene. The conversion of $(C_5H_5)_2TiSe_5$ to its alkene diselenide derivative was characterized as a function of reactant concentrations and temperature. In refluxing 1,2-dichloroethane solution, this reaction was found to be first order with respect to both acetylene and pentaselenide concentrations, the second-order rate constant being 1.58×10^{-3} M^{-1} s^{-1} at 83.5 °C. The compounds $(C_5H_4R)_2TiE_2C_2Z_2$ were found to react with a variety of dichloro compounds, L_nMCl_2, to give the ligand-exchange products $L_nME_2C_2Z_2$ (Z = CO_2CH_3) and $(C_5H_4R)_2TiCl_2$. In this way the following new compounds were prepared: $Ni(Se_2C_2Z_2)(Ph_2PCH_2CH_2CH_2PPh_2)$, Pt-$(E_2C_2Z_2)(PPh_3)_2$ (E = S, Se), $Pt_2(Se_2C_2Z_2)_2(Ph_2PC_2PPh_2)$, $(AsPh_4)[Rh(Se_2C_2Z_2)(CO)_2]$, and $SCSe_2C_2Z_2$. Alcoholysis of $(C_5H_5)_2TiSe_2C_2(CO_2CH_3)_2$ in basic methanol gave solutions of $Na_2Se_2C_2(CO_2CH_3)_2$, which was derivatized with CH_3I (2 equiv) and *cis*-$PtCl_2(PPh_3)_2$.

Introduction

Transition-metal complexes containing polysulfido chelates have been recognized since the report of the $(NH_4)_2PtS_{15}$ structure in 1967.[1] This compound, whose synthesis was first described in 1903,[2] is composed of octahedral platinum(IV) coordinated to three bidentate S_5^{2-} chelates. In recent years several other examples of penta- and tetrasulfido metal chelates have been prepared although generally not by design. Those characterized crystallographically include $(C_5H_5)_2MS_5$ (M = Ti,[3,4] V[4]), $(C_5H_5)_2MS_4$ (M = Mo,[5a] W[5b]), $(Ph_4P)_2Fe_2(\mu$-$S)_2(S_5)_2$,[6a] $(Ph_4P)_2Mo(S)_2(\mu$-$S)_2FeS_5$,[6b] $(Et_4N)_2MoS(S_4)_2$,[7a] $Mo_2(\mu$-$S)_2(S)_2(S_2)(S_4)$,[7b] $(C_5H_5)Co(S_5)PMe_3$,[8] NH_4CuS_4,[9]
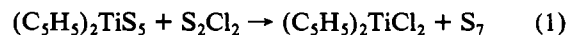
Scheme I[a]

^{a} Cp = η^5-C_5H_4R (R = H or CH_3).

$Os_2(Et_2NCS_2)_3(Et_2NCS_3)(\mu$-$S_5)$,[10] and $(NH_4)_2PdS_{11}$.[11]

Of the polysulfido chelates, the reactivity of only $(C_5H_5)_2TiS_5$ and $(NH_4)_2PtS_{15}$ have been examined. For the titanium complex two reactivity patterns have been elucidated: transfer of an S_5 unit to nonmetal halides and sulfur abstraction concomitant with rearrangement. Illustrative of the first of these is the synthesis of *cyclo*-S_7 from $(C_5H_5)_2TiS_5$ and S_2Cl_2 (eq 1),[12] a process that exploits the halophilicity of the

$$(C_5H_5)_2TiS_5 + S_2Cl_2 \rightarrow (C_5H_5)_2TiCl_2 + S_7 \qquad (1)$$

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