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New heterobimetallic compounds derived from [η^5-(dimethylphosphino)cyclopentadienyl]-[η^7-(dimethylphosphino)cycloheptatrienyl]titanium

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Abstract

The dimetalation of (η^5-C_5H_5)(η^7-C_7H_7)Ti with n-BuLi/TMEDA produces (η^5-C_5H_4Li)(η^7-C_7H_6Li)Ti·2TMEDA (3) in 61% yield as a highly air-sensitive solid. Treatment of 3 with Me_2PCl affords (η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti (2) as a highly air-sensitive green solid in 86% yield. Reactions between 2 and $M(CO)_6$ (M = Cr, Mo) in refluxing xylene result in the formation of chelated heterobimetallic compounds [(η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti]$M(CO)_4$ (M = Cr, Mo) in high yields, whereas a reaction between 2 and $Fe_2(CO)_9$ under similar conditions yields the non-chelated product [(η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti][$Fe(CO)_4$]$_2$. Treatment of bis(1,5-cyclooctadiene)nickel with 2 equivalents of 2 in toluene at room temperature results in displacement of both COD ligands and formation of a nickel(0) complex [(η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti]$_2$Ni in 78% yield. The ^1H and ^{31}P NMR spectra of these new heterobimetallics have been studied in detail. The crystal structure of [(η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti]$Cr(CO)_4$ (4) has been determined. It crystallizes in $Pn2_1a$ with $a = 16.603(9)$, $b = 24.674(9)$, $c = 10.887(3)$ Å, and $D_{calc} = 1.45$ g cm^{-3} for $Z = 8$. The two independent molecules differ by the relative twist of the ring carbon atoms carrying the phosphine ligands. Average parameters include Ti–C(η^7) = 2.19(2) Å, Ti–C(η^5) = 2.31(1) Å, Cent–Ti–Cent = 175.8°, Cr–P = 2.39(1) Å.

Introduction

Heterobimetallic compounds in which the metals are held in close proximity have been extensively studied in recent years, in connection with probing potential electronic and chemical interactions between the metal centers [1,2]. Metallocenes that are substituted with two phosphino ligands are useful in this regard, since they can be converted into heterobimetallic derivatives by reactions with metal carbonyls or transition metal halides [3–12].

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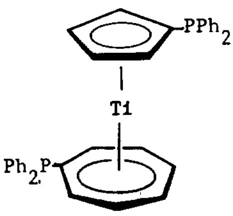
We have recently reported the synthesis of the new bidentate organometallic compound [η^5-(diphenylphosphino)cyclopentadienyl][η^7-(diphenylphosphino)cycloheptatrienyl]titanium (**1**), and its reactions with a variety of metal carbonyls, leading to chelated heterobimetallic compounds [13].



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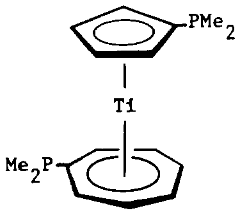

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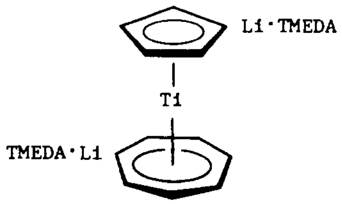
In the present article, these studies are extended to include the formation of the dimethylphosphino analog (**2**), and reactions of **2** leading to new heterobimetallic derivatives containing Cr, Mo, Fe and Ni. An X-ray structural study of a tetracarbonylchromium complex of **2** has been undertaken, and the results are compared with an analogous derivative of **1**.

Results and discussion

We have previously reported that the organotitanium sandwich compound (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium can be readily dimetalated by n-butyllithium-TMEDA (TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) and that the resulting dilithium derivative (**3**) upon further reaction with chlorodiphenylphosphine afforded **1** in high yield [13]. In earlier studies, we were able to successfully isolate and characterize a related organolithium compound, 1,1'-dilithioferrocene · 2 TMEDA [14]. In a similar manner, a reaction between (η^5-C_5H_5)(η^7-C_7H_7)Ti and 2.5 equivalents of n-butyllithium-TMEDA in hexane solution afforded **3** as a dark brown, highly air-sensitive solid in 61% yield. Several attempts to prepare an analytically pure sample of **3**, as was accomplished in the case of 1,1'-dilithioferrocene · 2TMEDA [14], were not successful. Consistently low carbon/hydrogen values were obtained even after the sample had been thoroughly washed and dried under vacuum. On the other hand, the ^1H NMR spectrum of **3** in



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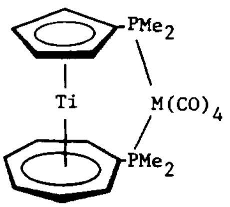

4 M = Cr

5 M = Mo

THF-d_8 solution was consistent with the proposed structure, and suggested the incorporation of 2 TMEDA ligands as was found for 1,1′-dilithioferrocene · 2 TMEDA [14,15 *]. Solid **3** could be stored without decomposition in a glove box under nitrogen or argon for extended periods of time, and has proved to be a valuable intermediate in the synthesis of a variety of heteroannularly disubstituted derivatives of $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$ [16].

A subsequent reaction between dilithium reagent **3** and two equivalents of chlorodimethylphosphine in hexane/diethyl ether solution produced **2** in 86% yield. Diphosphine **2** was characterized by elemental analysis and by its ^1H NMR and mass spectra. The latter displayed a moderately intense molecular ion peak at *m/e* 324 and a base peak corresponding to loss of two $(CH_3)_2P$ units from M^+. The ^{31}P NMR spectrum of **2** in toluene-d_8 exhibited two sharp singlets at δ −22.8 and −58.4 ppm, corresponding to phosphorus atoms attached to the C_7- and C_5-rings, respectively, in **3**. These assignments can be made with confidence, since the ^{31}P NMR spectrum of $(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_7)Ti$ occurs as a singlet at δ −56.8 ppm [16]. In the case of **1**, the ^{31}P NMR spectrum in toluene-d_8 shows singlets at δ 17.9 and −18.3 ppm, again corresponding to phosphorus atoms attached to the respective C_7- and C_5-rings in **1**. To confirm these assignments, we measured the ^{31}P NMR spectrum of the known compound $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_6PPh_2)Ti$ [17] and observed a single sharp resonance at δ 17.4 ppm. Both phosphorus nuclei are clearly much more deshielded in **1** compared to **2**.

Diphosphine **2** was highly air-sensitive compared to **1** and also much more reactive. For example, it decomposed upon attempted chromatography on alumina under argon, whereas **1** could be successfully chromatographed under these conditions. This result made purification of **2** much more difficult than in the case of **1**. ^1H NMR analysis indicated that preparations of **2** were occasionally contaminated with small amounts of $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$, however, this did not present separation problems in subsequent reactions of **2**.

Reactions of diphosphine **2** with $Cr(CO)_6$ or $Mo(CO)_6$ in refluxing toluene afforded the corresponding new heterobimetallic compounds (**4**, **5**) in yields of 97 and 90%, respectively. Both **4** and **5** were isolated as dark green crystals after column chromatography and subsequent crystallization. Both compounds were very air-sensitive, in contrast to their diphenylphosphino analogs [13], although they could be stored for long periods of time under argon in a glovebox. Both new heterobimetallics were characterized by NMR, IR and mass spectral methods as well as by elemental analyses. The mass spectra of **4** and **5** exhibited weak molecular ion peaks as well as fragmentation peaks resulting from losses of the carbonyl substituents.

The ^{31}P NMR resonances of the two non-equivalent phosphorus nuclei in both **4** and **5** were shifted to lower field compared to the analogous resonances for **2**. Moreover, the two phosphorus resonances for each compound appeared as *doublets* (**4**, $J(P\text{-}P) = 37.4$ Hz; **5**, $J(P\text{-}P) = 30.7$ Hz). These results provide strong evidence that the dimethylphosphino substituents in both **4** and **5** are coordinated to the same metal atom, a conclusion that has been corroborated by an X-ray structural study on **4** (vide infra).

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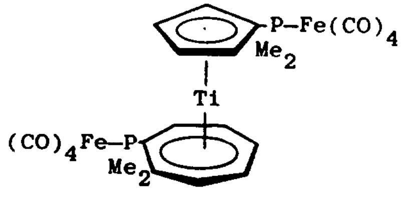
* A reference number with an asterisk indicates a note in the list of references.

A reaction between **2** and $Fe_2(CO)_9$ in refluxing toluene followed by chromatographic separation and crystallization led to the bis(tetracarbonyliron) product (**6**) in 70% yield. The IR spectrum of **6** exhibited characteristic bands at 2045, 1968 and 1930 cm^{-1}, whereas the ^{31}P NMR spectrum of **6** contained two *singlet* resonances at δ 34.2 and 61.0 ppm. The mass spectrum of **6** exhibited a weak peak corresponding to the molecular ion at *m/e* 660 as well as fragmentation peaks due to successive losses of the 8 carbonyl ligands. The formation of **6** from **2** and $Fe_2(CO)_9$ is in contrast to a reaction between **1** and $Fe_2(CO)_9$, which under similar conditions produces primarily the corresponding $Fe(CO)_3$-bridged product [13].



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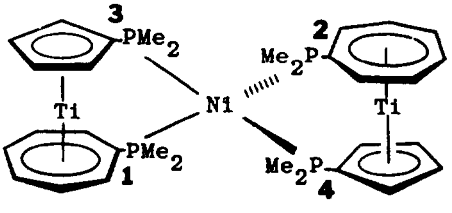

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Treatment of bis(1,5-cyclooctadiene)nickel with 2 equivalents of **2** in toluene at room temperature resulted in displacement of both COD ligands and formation of the nickel(0) complex **7** in 78% yield. The heterobimetallic complex **7** was crystallized from toluene/hexane as a fine blue-black solid. The product was very air-sensitive in the solid state and extremely so in solution. In the ^1H NMR spectrum of **7**, the dimethylphosphino substituents occurred as four broad singlets of equal intensity at δ 1.41, 1.45, 1.70 and 1.77 ppm, indicating four non-equivalent methyl substituents. The ^{31}P NMR spectrum of **7** exhibited 2 apparent triplets at δ -16.8 and 11.9 ppm, suggesting an AA'BB' spin pattern. Subsequent computer simulation studies by Bitterwolf and Wheeler [18] have indicated the following P–P coupling constants: $J(1\text{-}3) = J(2,4) = 25.0$ Hz, $J(1\text{-}4) = J(2\text{-}3) = 33.5$ Hz, $J(1,2) = 11.5$ Hz, and $J(3,4) = 22.6$ Hz.

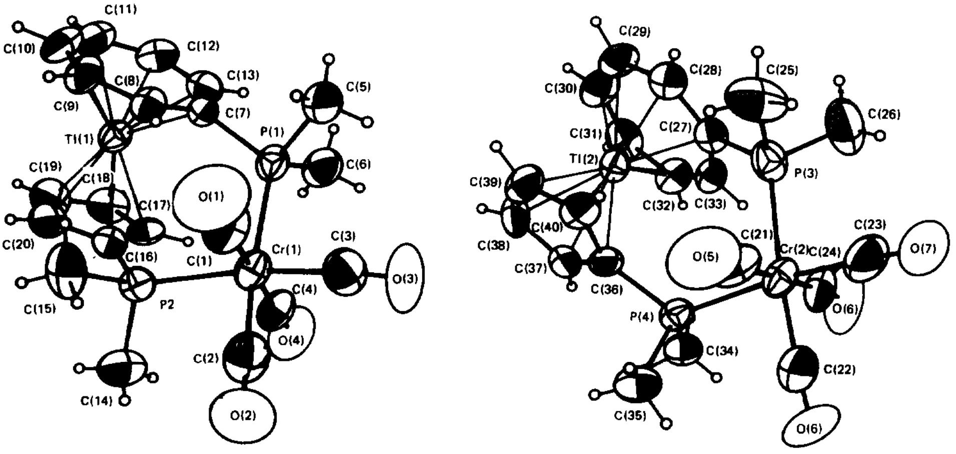

Fig. 1. Molecular structure and atom-labeling scheme for the two independent molecules of **4**.

During the course of our studies in this area, a related complex was reported by Elschenbroich and coworkers [12]. Their product, $[(\eta^6\text{-}C_6H_5PMe_2)_2Cr]_2Ni$, was characterized by spectral as well as X-ray structural analyses, and was shown to have a NiP_4-tetrahedron as the central unit. Earlier structural studies by Karsch et al. [19] on the complex $[(\eta^5\text{-}C_5H_5)_2Zr(CH_2PMe_2)_2]_2Ni$ likewise indicated 2 bidentate $(\eta^5\text{-}C_5H_5)_2Zr(CH_2PMe_2)_2$ molecules acting as chelating ligands to a tetrahedral Ni(0) center. Although we have not been able to grow suitable single crystals of 7 for an analogous X-ray structural investigation, 7 most likely has a structure similar to these Cr/Ni and Zr/Ni heterobimetallics, except that it contains non-equivalent C(5)- and C(7)-membered rings connected by titanium atoms.

X-Ray crystallographic studies

The molecular structure of the two independent molecules of $[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti]Cr(CO)_4$ (4) are depicted in Fig. 1, while bond distances and angles are given in Table 1. The two molecules differ in the relative twist of the ring carbon atoms bonded to the phosphines. In molecule 1, the P–C(η^7)–C(η^5)–P torsion angle is 38.9°, while in molecule 2 it is $-37.1°$. The absolute values are nearly identical to the 36° found in the diphenylphosphino analog, $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]Cr(CO)_4$ [13]. The smaller, less bulky methyl groups apparently allow the different packing modes observed. Despite this difference and the differing phosphine substituents, the bonding in the titanium sandwich portion of the molecules is identical. The average values include: Ti–C(η^5) = 2.30(1) (molecule 1 PMe_2 compound), 2.31(1) (molecule 2 PMe_2 compound), 2.31(2) Å (PPh_2 analog); Ti–Cent(η^5) = 1.97, 1.98, 1.98 Å; Ti–C(η^7) = 2.20(2), 2.19(2), 2.19(1) Å; Ti–Cent(η^7) = 1.47, 1.46, 1.46 Å; Cent–Ti–Cent = 175.2, 176.3, 173.5°.

In both the PMe_2 and PPh_2 compounds, the bond between Cr and the P bonded to the C_7 ring is longer than that to the other phosphine by just over 3σ. The actual values for the PMe_2 analog are shorter than observed for the PPh_2 compound: Cr–P(C_7) = 2.398(2)(PMe_2), 2.395(3)(PMe_2), 2.445 Å(PPh_2); Cr–P(C_5) = 2.380(2), 2.368(2), 2.415(3) Å. In all three molecules the Cr–carbonyl distances *trans* to the longer Cr–P distances are shorter than those *trans* to the remaining Cr–P bonds, however, these differences are just at or under the 3σ level.

The PMe_2 analog provides another example of the insensitivity of the titanium sandwich structure to coordination of the phosphine ligands. The C_7 rings are planar to within 0.029 Å and the P atoms deviate an average of 0.261 Å out of this plane toward Ti. The C_5 rings are planar to 0.006 Å with the P atoms bending 0.092 Å away from Ti. Similar values of 0.19 Å toward Ti(C_7–P) and 0.09 Å away from Ti(C_5–P) were observed in the PPh_2 compound.

Experimental

All operations were carried out under an argon atmosphere using Schlenk or glove box techniques except where specified. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and phosphorus pentoxide. Hexane, toluene, benzene and diethyl ether were distilled under argon from sodium–potassium alloy. Dichloromethane was distilled under argon from calcium hydride. *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was obtained from Aldrich

Table 1

Bond distances (Å) and angles (deg) for (η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti[Cr(CO)$_4$] (4)

Bond distances			
Cr(1)-P(1)	2.398(2)	Cr(1)-P(2)	2.380(2)
Cr(1)-C(1)	1.88(1)	Cr(1)-C(2)	1.84(1)
Cr(1)-C(3)	1.823(9)	Cr(1)-C(4)	1.880(9)
Ti(1)-C(7)	2.168(7)	Ti(1)-C(8)	2.172(7)
Ti(1)-C(9)	2.194(8)	Ti(1)-C(10)	2.216(9)
Ti(1)-C(11)	2.227(9)	Ti(1)-C(12)	2.213(8)
Ti(1)-C(13)	2.186(8)	Ti(1)-C(16)	2.299(7)
Ti(1)-C(17)	2.297(8)	Ti(1)-C(18)	2.32(1)
Ti(1)-C(19)	2.317(9)	Ti(1)-C(20)	2.292(8)
P(1)-C(5)	1.81(1)	P(1)-C(6)	1.812(9)
P(1)-C(7)	1.836(7)	P(2)-C(14)	1.807(9)
P(2)-C(15)	1.795(9)	P(2)-C(16)	1.799(7)
O(1)-C(1)	1.12(1)	O(2)-C(2)	1.18(1)
O(3)-C(3)	1.16(1)	O(4)-C(4)	1.11(1)
C(7)-C(8)	1.42(1)	C(7)-C(13)	1.42(1)
C(8)-C(9)	1.41(1)	C(9)-C(10)	1.43(1)
C(10)-C(11)	1.36(1)	C(11)-C(12)	1.41(1)
C(12)-C(13)	1.43(1)	C(16)-C(17)	1.42(1)
C(16)-C(20)	1.42(1)	C(17)-C(18)	1.42(1)
C(18)-C(19)	1.38(1)	C(19)-C(20)	1.41(1)
Cr(2)-P(3)	2.395(3)	Cr(2)-P(4)	2.368(2)
Cr(2)-C(21)	1.90(1)	Cr(2)-C(22)	1.85(1)
Cr(2)-C(23)	1.812(9)	Cr(2)-C(24)	1.84(1)
Ti(2)-C(27)	2.172(7)	Ti(2)-C(28)	2.177(8)
Ti(2)-C(29)	2.215(8)	Ti(2)-C(30)	2.210(9)
Ti(2)-C(31)	2.197(9)	Ti(2)-C(32)	2.207(8)
Ti(2)-C(33)	2.156(8)	Ti(2)-C(36)	2.317(7)
Ti(2)-C(37)	2.308(7)	Ti(2)-C(38)	2.335(9)
Ti(2)-C(39)	2.298(9)	Ti(2)-C(40)	2.304(8)
P(3)-C(25)	1.84(1)	P(3)-C(26)	1.83(1)
P(3)-C(27)	1.818(7)	P(4)-C(34)	1.839(9)
P(4)-C(35)	1.810(9)	P(4)-C(36)	1.805(7)
O(5)-C(21)	1.16(1)	O(6)-C(22)	1.14(1)
O(7)-C(23)	1.17(1)	O(8)-C(24)	1.17(1)
C(27)-C(28)	1.43(1)	C(27)-C(33)	1.44(1)
C(28)-C(29)	1.39(1)	C(29)-C(30)	1.40(1)
C(30)-C(31)	1.42(1)	C(31)-C(32)	1.42(1)
C(32)-C(33)	1.42(1)	C(36)-C(37)	1.43(1)
C(36)-C(40)	1.42(1)	C(37)-C(38)	1.40(1)
C(38)-C(39)	1.42(1)	C(39)-C(40)	1.38(1)
Ti(1)-Cent1	1.47	Ti(1)-Cent2	1.97
Ti(2)-Cent3	1.46	Ti(2)-Cent4	1.98
Bond angles			
P(1)-Cr(1)-P(2)	99.45(8)	P(1)-Cr(1)-C(1)	88.9(3)
P(2)-Cr(1)-C(1)	92.5(3)	P(1)-Cr(1)-C(2)	173.7(3)
P(2)-Cr(1)-C(2)	86.8(3)	C(1)-Cr(1)-C(2)	90.0(4)
P(1)-Cr(1)-C(3)	88.2(3)	P(2)-Cr(1)-C(3)	171.7(3)
C(1)-Cr(1)-C(3)	90.8(4)	C(2)-Cr(1)-C(3)	85.6(4)
P(1)-Cr(1)-C(4)	91.9(3)	P(2)-Cr(1)-C(4)	87.9(3)
C(1)-Cr(1)-C(4)	179.0(4)	C(2)-Cr(1)-C(4)	89.1(4)
C(3)-Cr(1)-C(4)	88.7(4)	Cr(1)-P(1)-C(5)	112.6(3)
Cr(1)-P(1)-C(6)	114.5(3)	C(5)-P(1)-C(6)	100.0(4)
Cr(1)-P(1)-C(7)	120.9(2)	C(5)-P(1)-C(7)	101.2(4)

Table 1 (continued)

C(6)-P(1)-C(7)	104.8(4)	Cr(1)-P(2)-C(14)	111.5(3)
Cr(1)-P(2)-C(15)	116.2(3)	C(14)-P(2)-C(15)	101.0(4)
Cr(1)-P(2)-C(16)	121.6(2)	C(14)-P(2)-C(16)	100.8(4)
C(15)-P(2)-C(16)	102.8(4)	Cr(1)-C(1)-O(1)	176.8(8)
Cr(1)-C(2)-O(2)	179.1(9)	Cr(1)-C(3)-O(3)	174.9(8)
Cr(1)-C(4)-O(4)	176.2(8)	P(1)-C(7)-C(8)	113.0(5)
P(1)-C(7)-C(13)	120.1(6)	C(8)-C(7)-C(13)	126.7(7)
C(7)-C(8)-C(9)	129.1(7)	C(8)-C(9)-C(10)	128.8(8)
C(9)-C(10)-C(11)	129.4(8)	C(10)-C(11)-C(12)	127.7(8)
C(11)-C(12)-C(13)	129.5(8)	C(7)-C(13)-C(12)	128.7(7)
P(2)-C(16)-C(17)	126.0(6)	P(2)-C(16)-C(20)	128.3(6)
C(17)-C(16)-C(20)	105.5(6)	C(16)-C(17)-C(18)	108.6(7)
C(17)-C(18)-C(19)	108.3(7)	C(18)-C(19)-C(20)	108.1(7)
C(16)-C(20)-C(19)	109.5(7)	P(3)-Cr(2)-P(4)	99.74(8)
P(3)-Cr(2)-C(21)	90.4(3)	P(4)-Cr(2)-C(21)	87.9(3)
P(3)-Cr(2)-C(22)	174.2(3)	P(4)-Cr(2)-C(22)	86.1(3)
C(21)-Cr(2)-C(22)	89.7(4)	P(3)-Cr(2)-C(23)	87.1(3)
P(4)-Cr(2)-C(23)	173.1(3)	C(21)-Cr(2)-C(23)	91.3(5)
C(22)-Cr(2)-C(23)	87.1(4)	P(3)-Cr(2)-C(24)	90.4(3)
P(4)-Cr(2)-C(24)	92.5(3)	C(21)-Cr(2)-C(24)	179.0(4)
C(22)-Cr(2)-C(24)	89.4(5)	C(23)-Cr(2)-C(24)	88.2(5)
Cr(2)-P(3)-C(25)	113.4(3)	Cr(2)-P(3)-C(26)	113.2(3)
C(25)-P(3)-C(26)	99.4(5)	Cr(2)-P(3)-C(27)	121.9(3)
C(25)-P(3)-C(27)	105.3(4)	C(26)-P(3)-C(27)	100.7(4)
Cr(2)-P(4)-C(34)	116.7(3)	Cr(2)-P(4)-C(35)	111.2(3)
C(34)-P(4)-C(35)	100.8(4)	Cr(2)-P(4)-C(36)	122.5(2)
C(34)-P(4)-C(36)	101.3(4)	C(35)-P(4)-C(36)	101.1(4)
Cr(2)-C(21)-O(5)	178.8(8)	Cr(2)-C(22)-O(6)	176.2(9)
Cr(2)-C(23)-O(7)	176.9(9)	Cr(2)-C(24)-O(8)	176.1(9)
P(3)-C(27)-C(28)	121.7(6)	P(3)-C(27)-C(33)	113.7(5)
C(28)-C(27)-C(33)	124.3(7)	C(27)-C(28)-C(29)	130.7(7)
C(28)-C(29)-C(30)	129.4(8)	C(29)-C(30)-C(31)	128.3(7)
C(30)-C(31)-C(32)	128.6(8)	C(31)-C(32)-C(33)	127.4(8)
C(27)-C(33)-C(32)	131.1(7)	P(4)-C(36)-C(37)	128.3(6)
P(4)-C(36)-C(40)	125.4(6)	C(37)-C(36)-C(40)	106.2(6)
C(36)-C(37)-C(38)	109.5(7)	C(37)-C(38)-C(39)	105.9(7)
C(38)-C(39)-C(40)	110.2(8)	C(36)-C(40)-C(39)	108.2(7)
Cent1-Ti(1)-Cent2	175.3	Cent3-Ti(2)-Cent4	176.3

Chemical Co. and was dried and distilled from calcium hydride. Column chromatography was carried out under argon using CAMAG alumina. The alumina was heated under vacuum on a rotary evaporator to remove oxygen and water, then deactivated with 5% (by weight) of argon-saturated water and stored under argon until used.

$(CH_3)_2PCl$, $Fe_2(CO)_9$, $Mn_2(CO)_{10}$ and $Ni(1,5\text{-}C_8H_{12})_2$ were obtained from Strem Chemicals, Inc., whereas $Cr(CO)_6$ and $Mo(CO)_6$ were purchased from Pressure Chemical Co. (η^5-Cyclopentadienyl)(η^7-cycloheptatrienyl)titanium was prepared by a literature procedure [17,20]. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer, whereas ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer. IR spectra were obtained on a Perkin-Elmer 1310 spectrometer. Mass spectra were obtained at 70 eV on a Varian CH7 mass spectrometer at the University of Bayreuth, Bayreuth, West Germany. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

(η^5-Lithiocyclopentadienyl)(η^7-lithiocycloheptatrienyl)titaniumbis(N,N,N',N'*-tetramethylethylenediamine) (3)*

Into an argon-purged 500-ml Schlenk flask were placed 150 ml of hexane and 7.6 ml (50.4 mmol) of TMEDA, and the solution was cooled to $-30\,^\circ$C and stirred for 30 min. Subsequent addition of n-butyllithium in hexane (16.8 ml, 42 mmol) produced a light yellow solution. Meanwhile, a blue suspension of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (3.4 g, 16.7 mmol) in 100 ml of hexane was prepared in an argon-purged 200-ml Schlenk flask at $-30\,^\circ$C and stirred for 30 min. The latter suspension was transferred via a cannula to the n-BuLi · TMEDA solution very slowly over ca. 1 h. Stirring was continued at $-30\,^\circ$C for 3 h and the reaction mixture was then allowed to warm to room temperature and stirred for an additional 5 h. During this time, the slurry changed from blue to brown-black. The fine brown-black solid was collected on a frit under argon, washed with hexane several times until the washings were colorless, and then dried under vacuum at room temperature to afford 4.53 g (61%) of **3** as a highly air-sensitive, pyrophoric powder. (Found: C, 62.94; H, 7.80. $C_{24}H_{42}Li_2N_4Ti$ calcd.: C, 64.29; H, 9.44%).

(η^5-Dimethylphosphinocyclopentadienyl)(η^7-dimethylphosphinocycloheptatrienyl)titanium (2)

A brown-black suspension of (η^5-lithiocyclopentadienyl)(η^7-lithiocycloheptatrienyl)titanium · 2 TMEDA (4.41 g, 9.84 mmol) in 250 ml of hexane was prepared in a 500-ml Schlenk flask which had been cooled to $-78\,^\circ$C, and the mixture was stirred for 30 min. To this suspension was added chlorodimethylphosphine [21*] (2.0 g, 20.8 mmol) dropwise via an addition funnel over a period of 2 h. After the addition, 20 ml of diethyl ether was added and the reaction mixture was allowed to warm to room temperature over a 3 h period. Stirring was continued at room temperature overnight. The solvent was then removed under reduced pressure to afford a green oil. This residue was extracted with hot hexane and filtered to give a dark green solution. The solution was concentrated under reduced pressure at room temperature to ca. one-half volume and slowly cooled to $0\,^\circ$C to afford **2** as a green solid (2.74 g, 86%). An analytical sample was prepared by several recrystallizations from hexane. (Found: C, 59.97; H, 6.52. $C_{16}H_{22}P_2Ti$ calcd.: C, 59.28; H, 6.84%). ^{1}H NMR (toluene-d_8) δ 1.00 (d, 6 H, C_5-$P(CH_3)_2$, J(H–P) = 3.7 Hz), 1.27 (d, 6 H, C_7-$P(CH_3)_2$, J(H–P) = 4.3 Hz), 5.05 (m, 4 H, C_5H_4), 5.44–5.90 (m, 6 H, C_7H_6). ^{31}P NMR (toluene-d_8) δ -58.4 (s, C_5-P), -22.8 (s, C_7-P). MS m/e 324 (18, M^+), 309 (25, $M-CH_3)^+$, 264 (13, $M-4CH_3)^+$, 204 (100, $M-2P(CH_3)_2)^+$.

[(η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti]Cr(CO)$_4$ (4)

Into an argon-purged 100-ml Schlenk flask were placed 0.50 g (1.54 mmol) of (η^5-$C_5H_4PMe_2$)(η^7-$C_7H_6PMe_2$)Ti, 0.33 g (1.50 mmol) of $Cr(CO)_6$, and 60 ml of toluene. The mixture was heated to reflux with stirring for 51 h, then filtered while hot through a frit. The solvent was removed and the residue was chromatographed on a dry-packed alumina column. Elution with hexane removed a small blue band that contained (η^5-C_5H_5)(η^7-C_7H_7)Ti. Continued elution with hexane/toluene (1 : 1) produced a green band which upon evaporation of the solvent yielded 0.71 g (97%) of $[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti]Cr(CO)_4$ as a green solid. An analytical sample was prepared by recrystallization from dichloromethane/hexane to produce **4** as dark green crystals. (Found: C, 49.21; H, 4.66. $C_{20}H_{22}CrO_4P_2Ti$ calcd.: C, 49.20; H, 4.54%). IR (CH_2Cl_2) ν(CO) 2000 (s), 1882 (vs, br) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.62 (d, 6 H, $C_5\text{-}P(CH_3)_2$, $J(H\text{-}P) = 6.6$ Hz), 1.91 (d, 6 H, $C_7\text{-}P(CH_3)_2$, $J(H\text{-}P) = 6.4$ Hz), 5.33 (m, 2 H, C_5H_4), 5.40 (m, 2 H, C_5H_4), 5.52–5.80 (m, 6 H, C_7H_6). ^{31}P NMR ($CDCl_3$) δ 13.4, (d, C_5-P, $J(P\text{-}P) = 37.4$ Hz), 39.3 (d, C_7-P, $J(P\text{-}P) = 37.4$ Hz). MS m/e 488 (7, M^+), 460 (2, $M - CO)^+$, 414 (2, $M - 3CO)^+$, 376 (100, $M - 4CO)^+$.

$[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti]Mo(CO)_4$ (5)

$(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti$ (0.50 g, 1.54 mmol), $Mo(CO)_6$ (0.39 g, 1.50 mmol) and toluene (60 ml) were added to a 100-ml Schlenk flask under argon. The solution was heated to reflux for 5 h, filtered while hot, and the filtrate evaporated on a small amount of alumina under reduced pressure. The residue was added to a dry-packed column of alumina (1.5 × 5 cm). Hexane elution removed a small blue band that contained $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$. Elution with hexane/toluene (1 : 1) gave a green band that was collected under argon. The solvent was removed in vacuo to afford 0.72 g (90%) of $[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti]Mo(CO)_4$. An analytical sample was obtained by recrystallization from dichloromethane/hexane as dark green crystals. (Found: C, 44.85; H, 4.09. $C_{20}H_{22}MoO_4P_2Ti$ calcd.: C, 45.14; H, 4.17%). IR (CH_2Cl_2) ν(CO) 2010 (m), 1982 (s, br), 1870 (sh) cm^{-1}. ^1H NMR (toluene-d_8) δ 1.30 (d, 6 H, $C_5\text{-}P(CH_3)_2$, $J(H\text{-}P) = 5.9$ Hz), 1.57 (d, 6 H, $C_7\text{-}P(CH_3)_2$, $J(H\text{-}P) = 5.7$ Hz), 4.86 (m, 2 H, C_5H_4), 4.96 (m, 2 H, C_5H_4), 5.34–5.43 (m, 6 H, C_7H_6). ^{31}P NMR (toluene-d_8) δ −9.6 (d, C_5-P, $J(P\text{-}P) = 30.7$ Hz), 17.8 (d, C_7-P, $J(P\text{-}P) = 30.7$ Hz). MS m/e 532 (1, M^+), 476 (1, $M - 2CO)^+$, 420 (4, $M - 4CO)^+$, 204 (100, $M - 4CO - 2P(CH_3)_2 - Mo)^+$.

$[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti][Fe(CO)_4]_2$ (6)

Into an argon-flushed 100-ml Schlenk flask were placed $(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti$ (0.61 g, 1.87 mmol) and $Fe_2(CO)_9$ (0.69 g, 1.87 mmol) followed by 60 ml of toluene. The mixture was heated to reflux for 26 h and filtered while hot through a frit. The solvent was removed and the residue chromatographed on an alumina column (1.5 × 6 cm). Hexane elution produced a small blue band containing $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$, whereas elution with hexane/toluene (1 : 1) gave a green band. Removal of the solvent in vacuo produced 0.92 g (70%) of $[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti][Fe(CO)_4]_2$. Recrystallization of the product from dichloromethane/hexane afforded an analytically pure sample as light green crystals. (Found: C, 44.13; H, 3.48. $C_{24}H_{22}Fe_2O_8P_2Ti$ calcd.: C, 43.68; H, 3.66%). IR (CH_2Cl_2) ν(CO) 2045 (m), 1968 (m) and 1930 (s) cm^{-1}. ^1H NMR (toluene-d_8) δ 1.44 (d, 6 H, $C_5\text{-}P(CH_3)_2$, $J(H\text{-}P) = 10.2$ Hz), 1.59 (d, 6 H, $C_7\text{-}P(CH_3)_2$, $J(H\text{-}P) = 9.2$ Hz), 5.17 (m, 2 H, C_5H_4), 5.23 (m, 2 H, C_5H_4), 5.42–6.10 (m, 6 H, C_7H_6). ^{31}P NMR (toluene-d_8) δ 34.2 (s, C_5-P), 61.0 (s, C_7-P). MS m/e 660 (11, M^+), 632 (17, $M - CO)^+$, 576 (5, $M - 3CO)^+$, 548 (33, $M - 4CO)^+$, 520 (21, $M - 5CO)^+$, 492 (100, $M - 6CO)^+$, 464 (37, $M - 7CO)^+$, 436 (91, $M - 8CO)^+$, 380 ($M - 8CO - Fe)^+$, 320 (73, $M - 8CO - Fe - 2CH_3)^+$.

$[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti]_2Ni$ (7)

A 100-ml Schlenk flask was charged under argon with $(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti$ (0.79 g, 2.44 mmol), $Ni(1,5\text{-}C_8H_{12})_2$ (0.27 g, 0.98 mmol) and 70 ml of toluene. The flask was covered with aluminum foil and stirred in the dark at room temperature for 48 h. The solvent was then removed in vacuo to afford a blue-black oil. This residue was dissolved in a minimum amount of toluene and an excess of hexane was added, producing a blue-black precipitate. The solid was collected on a Celite plug on a frit. Addition of toluene gave a blue-black solution. The latter was concentrated under vacuum and cooled to −78 °C to afford 0.54 g (78%) of $[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti]_2Ni$ as a fine blue-black solid. An analytical sample was obtained by recrystallization of the product from toluene/hexane at −20 °C. (Found: C, 53.93; H, 6.13. $C_{32}H_{44}NiP_4Ti_2$ calcd.: C, 54.35; H, 6.27%). ^1H NMR (toluene-d_8) δ 1.41 (s(br), 6 H, $C_5\text{-}P(CH_3)_2$), 1.46 (s(br), 6 H, $C_5\text{-}P(CH_3)_2$), 1.70 (s(br), 6 H, $C_7\text{-}P(CH_3)_2$), 1.77 (s(br), 6 H, $C_7\text{-}P(CH_3)_2$), 5.07 (m, 4 H, C_5H_4),

Table 2

Crystal data and summary of intensity data collection and structure refinement

Compound	$[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti][Cr(CO)_4]$
Color/shape	red/parallelepiped
Formula weight	488.22
Space group	$Pn2_1a$
Temperature, °C	20
Cell constants [a]	
a, Å	16.603(9)
b, Å	24.674(9)
c, Å	10.887(3)
Cell volume, $Å^3$	4460.0
Formula units/unit cell	8
D_{calc}, g cm^{-3}	1.45
μ_{calc}, cm^{-1}	10.42
Diffractometer/scan	Enraf–Nonius CAD-4/ω–2θ
Radiation, graphite monochromator	Mo-K_α ($\lambda = 0.71073$)
Max crystal dimensions, mm	$0.25 \times 0.26 \times 0.35$
Scan width	$0.80 + 0.35 \tan\theta$
Standard reflections	800; 0, 12, 0; 008
Decay of standards	±3%
Reflections measured	3429
2θ range, deg	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	+19, +29, +13
Reflections observed $[F_o \geqslant 5\sigma(F_o)]$ [b]	2463
Computer programs [c]	SHELX [22]
Structure solution	SHELXS [23]
No. of parameters varied	527
Weights	$[\sigma(F_o)^2 + 0.00006\,F_o^2]^{-1}$
GOF	1.43
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	0.036
R_w	0.036
Largest feature final diff. map	0.2e$^-$ Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz-polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref. 24.

Table 3

Final fractional coordinates for $(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti[Cr(CO)_4]$ (4)

Atom	x	y	z	B_{eq} [a]
Cr(1)	0.95880(8)	0.2500	0.6753(1)	3.04
Ti(1)	0.96930(9)	0.20075(6)	0.2591(1)	2.71
P(1)	0.8519(1)	0.23147(9)	0.5334(2)	2.91
P(2)	1.0711(1)	0.23688(9)	0.5429(2)	2.79
O(1)	0.9560(6)	0.1334(3)	0.7555(8)	7.47
O(2)	1.0784(5)	0.2735(4)	0.8768(6)	7.83
O(3)	0.8387(4)	0.2770(4)	0.8688(7)	8.11
O(4)	0.9611(5)	0.3679(3)	0.6118(7)	6.29
C(1)	0.9574(6)	0.1766(4)	0.7221(8)	4.40
C(2)	1.0323(6)	0.2645(4)	0.7976(8)	4.67
C(3)	0.8825(6)	0.2660(4)	0.7901(8)	4.67
C(4)	0.9609(6)	0.3237(4)	0.6314(8)	3.68
C(5)	0.7726(5)	0.1905(4)	0.6003(9)	4.68
C(6)	0.7941(5)	0.2905(3)	0.4879(8)	4.38
C(7)	0.8711(4)	0.1947(3)	0.3897(6)	2.57
C(8)	0.9230(4)	0.1496(3)	0.4055(7)	2.68
C(9)	0.9578(5)	0.1157(3)	0.3157(8)	3.57
C(10)	0.9498(6)	0.1182(4)	0.1848(8)	3.86
C(11)	0.9061(5)	0.1532(4)	0.1144(8)	4.01
C(12)	0.8552(5)	0.1956(4)	0.1547(7)	3.56
C(13)	0.8397(5)	0.2145(3)	0.2769(7)	3.23
C(14)	1.1511(5)	0.2842(4)	0.5764(9)	4.66
C(15)	1.1234(6)	0.1735(4)	0.5580(8)	4.45
C(16)	1.0626(4)	0.2447(3)	0.3791(6)	2.63
C(17)	1.0161(5)	0.2845(3)	0.3170(7)	2.91
C(18)	1.0300(6)	0.2794(4)	0.1888(8)	3.97
C(19)	1.0836(5)	0.2377(4)	0.1703(7)	4.34
C(20)	1.1043(5)	0.2161(4)	0.2855(7)	3.54
Cr(2)	0.69482(8)	−0.04090(7)	0.6975(1)	3.30
Ti(2)	0.71892(8)	−0.00459(6)	0.2770(1)	2.52
P(3)	0.5934(1)	−0.0224(1)	0.5468(2)	3.46
P(4)	0.8109(1)	−0.03779(9)	0.5714(2)	2.59
O(5)	0.6843(5)	−0.1626(3)	0.6433(7)	6.65
O(6)	0.8044(5)	−0.0662(4)	0.9073(6)	7.73
O(7)	0.5641(4)	−0.0507(5)	0.8836(6)	9.59
O(8)	0.7089(6)	0.0771(3)	0.7632(8)	7.81
C(21)	0.6881(6)	−0.1163(4)	0.6626(8)	4.01
C(22)	0.7647(6)	−0.0556(4)	0.8254(9)	4.72
C(23)	0.6140(6)	−0.0460(5)	0.8086(8)	5.57
C(24)	0.7017(6)	0.0318(5)	0.7343(8)	4.92
C(25)	0.5306(6)	−0.816(4)	0.510(1)	5.35
C(26)	0.5151(6)	0.0237(5)	0.602(1)	6.54
C(27)	0.6175(4)	0.0084(3)	0.3996(6)	2.70
C(28)	0.5886(5)	−0.0138(3)	0.2864(7)	3.21
C(29)	0.6075(5)	−0.0008(4)	0.1654(7)	3.56
C(30)	0.6619(6)	0.0374(4)	0.1202(7)	4.24
C(31)	0.7097(5)	0.0750(4)	0.1874(8)	3.67
C(32)	0.7132(5)	0.0831(3)	0.3163(7)	3.56
C(33)	0.6728(5)	0.0530(3)	0.4083(7)	2.88
C(34)	0.8723(5)	0.0242(3)	0.5796(8)	3.57
C(35)	0.8840(5)	−0.0883(4)	0.6177(8)	4.39
C(36)	0.8069(4)	−0.0491(3)	0.4077(6)	2.69
C(37)	0.8531(4)	−0.0233(3)	0.3133(6)	3.21
C(38)	0.8343(5)	−0.0465(5)	0.1995(8)	4.70
C(39)	0.7749(6)	−0.0865(4)	0.2238(8)	4.13
C(40)	0.7585(5)	−0.0884(3)	0.3480(7)	3.23

[a] $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

5.29 (m, 4 H, C_5H_4), 5.49–5.64 (m, 8 H, C_7H_6), 5.79–5.96 (m, 4 H, C_7H_6). ^{31}P NMR (toluene-d_8) δ −16.8 (t, C_5-P), 11.9 (t, C_7-P).

X-ray data collection, structure determination and refinement for $[(\eta^5\text{-}C_5H_4PMe_2)(\eta^7\text{-}C_7H_6PMe_2)Ti]Cr(CO)_4$ *(4)*

A red single crystal of the title compound was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric *Pnma* or acentric $Pn2_1a$ (an alternate setting of $Pna2_1$) from the systematic absences. Subsequent solution and successful refinement of the structure was carried out in the acentric space group $Pn2_1a$. A summary of data collection parameters is given in Table 2. Least squares refinement with isotropic thermal parameters led to $R = 0.091$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ $Å^2$). Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.036$ and $R_w = 0.036$. The final values of the positional parameters are given in Table 3.

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References

1 R.M. Bullock and C.P. Casey, Acc. Chem. Res., 20 (1987) 167; see also references cited therein.
2 G.R. White and D.W. Stephan, Organometallics, 7 (1988) 903; see also references cited therein.
3 G.M. Whitesides, J.F. Gaasch and E.R. Stedronsky, J. Am. Chem. Soc., 94 (1972) 5258.
4 K.R. Mann, W.H. Morrison, Jr., and D.N. Hendrickson, Inorg. Chem., 13 (1974) 1180.
5 A.W. Rudie, D.W. Lichtenburg, M.L. Katcher and A. Davison, Inorg. Chem., 17 (1978) 2859.
6 W.R. Cullen, T.-J. Kim, F.W.B. Einstein and T. Jones, Organometallics, 2 (1983) 714; W.R. Cullen, T.-J. Kim and F.W.B. Einstein, Organometallics, 4 (1985) 346; I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig and J. Trotter, Organometallics, 4 (1985) 972.
7 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, and K. Hirotsu, J. Am. Chem. Soc., 106 (1984) 158; T. Hayashi, M. Kumada, T. Higuchi, and K. Hirotsu, J. Organomet. Chem., 334 (1987) 195; see also references cited therein.
8 T.A. George and R.C. Tisdale, J. Am. Chem. Soc., 107 (1985) 5157.
9 D.L. DuBois, C.W. Eigenbrot, Jr., A. Miedaner, J.C. Smart and R.C. Haltiwanger, Organometallics, 5 (1986) 1405.
10 W. Tikkanen, Y. Fugita and J.L. Peterson, Organometallics, 5 (1986) 888.
11 C. Elschenbroich and F. Stohler, Angew. Chem. Int. Ed. Engl., 14 (1975) 174.
12 C. Elschenbroich, G. Heikenfeld, M. Wünsch, W. Massa and G. Baum, Angew. Chem. Int. Ed. Engl., 27 (1988) 414.
13 L.B. Kool, M. Ogasa, M.D. Rausch and R.D. Rogers, Organometallics, 8 (1989) 1785.
14 M.D. Rausch, G.A. Moser and C.F. Meade, J. Organomet. Chem., 51 (1973) 1.

15 In several runs, integration of the TMEDA protons versus the C_5- and C_7-ring protons indicated a 1.5 : 1 ratio of the ligand to the dilithium compound, suggesting a mixture of mono- and di-TMEDA adducts was present.

16 M. Ogasa and M.D. Rausch, unpublished studies.

17 B. Demerseman, P.H. Dixneuf, J. Douglade and R. Mercier, Inorg. Chem., 21 (1982) 3942.

18 T.E. Bitterwolf and D. Wheeler, University of Idaho, personal communication, August, 1989.

19 H.H. Karsch, G. Muller and C. Kruger, J. Organomet. Chem., 273 (1984) 195.

20 B. Demerseman, Organomet. Synth., 3 (1986) 27.

21 $(CH_3)_2PCl$ is an extremely air-sensitive (pyrophoric) substance. It was stored in a small Schlenk tube under argon and carefully transferred to the addition funnel via a cannula.

22 G.M. Sheldrick, SHELX76, a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, England, 1976.

23 G.M. Sheldrick, SHELXS in G.M. Sheldrick, C. Kruger and R. Goddard (Eds.), Crystallographic Computing 3, Oxford University Press, 1985, pp. 175–189.

24 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974, pp. 72, 99, 149. (Present distributor: Kluwer Academic Publishers, Dordrecht and Boston).