(*P,P*-Dimethylphosphino)methyl Chromate(II) Complexes—$[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$, the First Homoleptic (Phosphino)methyl Transition Metal Complex

Dirk Steinborn,* Olaf Neumann, Clemens Bruhn, Tobias Rüffer, Roland Boese, and Frank W. Heinemann

Abstract: $[CrCl_2(thf)_2]$ reacts with $LiCH_2PMe_2$ in diethyl ether at $-50\,^{\circ}C$ to give $[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$ (**1**) as red, pyrophoric crystals ($T_{decomp} = 130-135\,^{\circ}C$; $\chi_g = 0.0096 \times 10^{-6}\,cm^3g^{-1}$, $\mu_{eff} = 0.81\,\mu_B/Cr$). Treatment of **1** with MeOD and S or with $LiAlD_4$ and S results in the formation of $S{=}PMe_2(CH_2D)$ (degree of deuteration > 95 %). Complex **1** reacts with *N,N,N',N'*-tetramethylethylenediamine (tmeda) to give $[\{Li(tmeda)\}_2Cr_2(CH_2PMe_2)_6]$ (**1a**) ($T_{decomp} = 140-145\,^{\circ}C$; $\chi_g = -0.834 \times 10^{-6}\,cm^3g^{-1}$) and $[\{Li_2Cr_2(CH_2PMe_2)_6(tmeda)\}_\infty]$ (**1b**). The structures of **1**, **1a**, and **1b** were determined by single-crystal X-ray analyses. They are dinuclear with short Cr–Cr quadruple bonds (193.9(1)–195.0(2) pm) that are bridged by two μ-η^2-CH_2PMe_2 ligands. Furthermore, each chromium atom is coordinated by two η^1-CH_2PMe_2 ligands. In complex **1** Li is coordinated by two P atoms, one O atom of a THF ligand, and one methylene C atom of the bridging CH_2PMe_2 ligand (Li coordination: P_2OC). In **1a** TMEDA acts as a bidentate chelate ligand, and in **1b** it acts as a bridging ligand forming a one-dimensional coordination polymer. Thus, Li coordinations P_2N_2 and P_2NC result in complexes **1a** and **1b**, respectively.

Keywords: C ligands · chromium · coordination modes · P ligands · structure elucidation

Introduction

The stability, reactivity, and structure of organometallic compounds with functionalized methyl ligands $L_xM{-}CH_2YR_n$ (L = ligand; M = metal; Y = Group 14–17 heteroelement; R = alkyl, aryl, H) are strongly dependent on the nature of the heteroatomic center, which can be i) neutral and coordinatively saturated (for example, $YR_n = SiR_3$, GeR_3, SnR_3), ii) neutral but Lewis basic (for example, $YR_n = NR_2$, PR_2, OR, SR, Cl), or iii) cationic (for example, $YR_n = {}^+NR_3$ ${}^+PR_3$, ${}^+SR_2$).[1] Complexes of type ii attract particular attention because the Lewis basic heteroatom is highly reactive in many cases and may open up the possibility of entirely new structures (for example, with η^2 coordination) and reactions (for example, carbenoid reactions). Usually this is exceptionally pronounced in homoleptic[2] complexes $[M(CH_2YR_n)_m]^{x-}$ ($x = 0, 1, 2, \ldots$), owing to the absence of any co-ligands (L).

Homoleptic complexes of types i ($YR_n = SiMe_3$, $GeMe_3$, $SnMe_3$)[3] and iii ($YR_n = {}^+PR_3$, ${}^+S(O)R_2$)[4] of many transition metals have been well characterized, but there are far fewer examples of type ii complexes, although homoleptic (amino)methyl complexes of all 3d elements ($YR_n = NC_5H_{10}$, NMe_2) have been synthesized and characterized.[5] Thiomethylnickel ($YR_n = SMe$, SPh, S(*t*Bu))[6] and palladium complexes ($YR_n =$ SPh)[7] have been described. Only $[\{Li(OEt_2)\}_2Ni(CH_2YR_n)_4]$ ($YR_n = NC_5H_{10}$,[5c] NMe_2,[5d] S(*t*Bu)[6]), $[\{Li(thf)\}_2Cr_2(CH_2NMe_2)_6]$,[5e] and $[\{Pd(CH_2SPh)_2\}_4]$ have been structurally characterized so far.[7]

Heteroleptic transition metal complexes of the type $[M(CH_2PR_2)_nL_m]^{x-}$ with co-ligands L such as phosphanes, carbonyl, and cyclopentadienyl are well known.[8] Homoleptic complexes ($m = 0$) are completely unknown. $[TaMe_3(CH_2PPh_2)_2]$ (isolated with tmeda impurities and characterized by ^1H NMR spectroscopy alone) is the only example of a (phosphino)methyl complex that contains no ligands other than σ-hydrocarbyl.[9] Taking into consideration a further functionalization, the homoleptic complex $[La\{\eta^3\text{-}CH(PPh_2)_2\}_3]$[10, 11] with bis(phosphino)methyl ligands bound in a π-allyl-like way was prepared. Silyl-substituted bis(phosphino)methyl anions form lanthanoid complexes in which the ligands are purely *P*-

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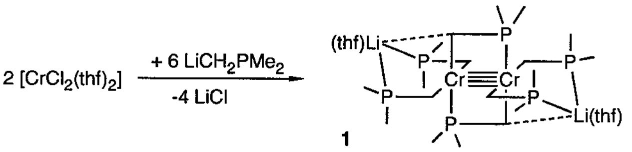
bonded, as in $[LiLa\{C(PMe_2)_2(SiMe_3)\}_4]$, or with *P*-bonded ligands and additional weak Ln···C interactions, as in $[Sc\{C(PMe_2)_2(SiMe_3)\}_3]$.[12, 13]

We report here the synthesis, characterization, and structure of a homoleptic (*P,P*-dimethylphosphino)methyl chromate(II) complex and its reaction with tmeda.

Results and Discussion

Synthesis and characterization of $[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$ (1): The reaction of the THF adduct of chromium(II) chloride with (*P,P*-dimethylphosphino)methyllithium[14] in diethyl ether at −50 °C yields a deep red solution from which red crystals of $[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$ (**1**) crystallize after addition of a small amount of THF in 80 % yield (Scheme 1).



Scheme 1. Synthesis of **1**.

The complex **1** is pyrophoric, but exhibits a relatively high thermal stability (T_{decomp} 130–135 °C). The sensitivity of **1** to moisture is low; it is soluble in diethyl ether, sparingly soluble in THF and in benzene, and insoluble in aliphatic hydrocarbons. The magnetic moment of **1** ($\chi_g = 9.6 \times 10^{-9}\,cm^3g^{-1}$ (295 K), $\mu_{eff} = 0.81\ \mu_B/Cr$) is consistent with a dinuclear d^4 Cr^{II} complex containing a Cr–Cr quadruple bond. Similar values for the residual paramagnetism μ_{eff} were found in other Cr^{II} complexes ($[\{Li(thf)\}_2Cr_2(CH_2NMe_2)_6]$ 0.67 μ_B/Cr,[5e] $[Li_2Cr_2(CH_2NC_5H_{10})_6]$ 0.96 μ_B/Cr,[5b] $[Cr_2(CH_2SiMe_3)_4(PMe_3)_2]$ 0.9 μ_B/Cr[15]); these might be explained in terms of a temperature-independent paramagnetism (TIP).[16]

Abstract in German: *$[CrCl_2(thf)_2]$ reagiert mit $LiCH_2PMe_2$ in Diethylether bei −50 °C zu $[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$ (1) (rote, pyrophore Kristalle, T_{Zers} 130–135 °C; $\chi_g = 0.0096 \times 10^{-6}\,cm^3g^{-1}$, $\mu_{eff} = 0.81\ \mu_B/Cr$). Die Reaktion mit MeOD und S sowie mit $LiAlD_4$ und S führt zur Bildung von $S{=}PMe_2(CH_2D)$ (Deuterierungsgrad > 95 %). Komplex **1** setzt sich mit tmeda zu den TMEDA Addukten $[\{Li(tmeda)\}_2Cr_2(CH_2PMe_2)_6]$ (**1a**) ($T_{Zers} = 140–145$ °C; $\chi_g = -0.834 \times 10^{-6}\,cm^3g^{-1}$) und $[\{Li_2Cr_2(CH_2PMe_2)_6(tmeda)\}_\infty]$ (**1b**) um. Die Strukturen aller drei Komplexe wurden durch Röntgenkristallstrukturanalyse ermittelt. Die Komplexe **1**, **1a** und **1b** sind dinuklear mit kurzen Cr–Cr-Vierfachbindungen (193.9(1)–195.0(2) pm), die durch zwei μ-η^2-CH_2PMe_2-Liganden überbrückt werden. Weiterhin befinden sich an jedem Chromatom zwei η^1-CH_2PMe_2-Liganden. In **1** ist Li durch zwei Phosphoratome, ein Sauerstoffatom eines THF Liganden und ein Methylen-Kohlenstoffatom des verbrückenden CH_2PMe_2-Liganden koordiniert (Li-Koordination: P_2OC). In **1a** fungiert TMEDA als zweizähniger Chelatligand und in **1b** als Brückenligand derart, daß sich ein eindimensionales Koordinationspolymer ergibt. Das führt in **1a** und **1b** zu Li-Koordinationen P_2N_2* bzw. *P_2NC.*

The molecular structure of **1** was confirmed by X-ray structure analysis (Figure 1, Table 1). Complex **1** crystallizes as discrete molecules without unusually short intermolecular contacts. The molecules reveal crystallographically imposed C_{2h} symmetry.

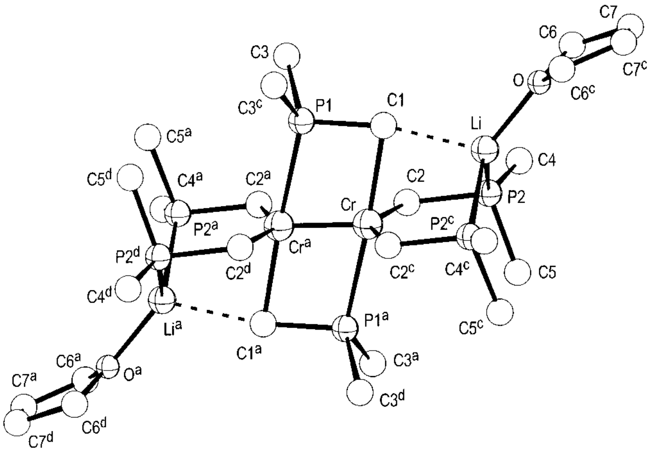


Figure 1. Molecular structure of $[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$ **1**, with numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [pm] and angles [°] for **1** with standard deviations in parentheses.

Cr–Cr^a	195.0(2)	C1-Cr-P1^a	177.0(1)
Cr–P1^a	239.5(1)	C2-Cr-C2^c	145.2(1)
Cr–C1	220.9(4)	Cr^a-Cr-P1^a	75.43(5)
Cr–C2	216.2(3)	Cr^a-Cr-C1	101.6(1)
P1–C1	179.9(4)	Li-C1-Cr	86.8(2)
P1–C3	182.5(3)	Cr-C1-P1	83.3(1)
P2–C2	180.0(3)	Cr-C2-P2	108.1(1)
P2–C4	183.9(4)	C1-P1-Cr^a	99.7(1)
P2–C5	183.7(3)	C3-P1-C3^c	99.6(3)
Li–C1	226.6(8)	C4-P2-C5	98.7(2)
Li–P2	254.9(4)	Li-P2-C2	96.4(2)
Li–O	191.9(7)	O-Li-P2	118.6(2)
		P2-Li-P2^c	110.1(3)

Symmetry transformation: a) $-x, y, -z$. c) $x, -y, z$.

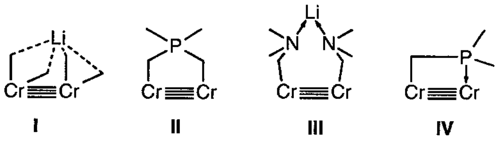
The Cr–Cr quadruple bond is short (195.0(2) pm) but not supershort (< 190 pm)[17] as in the homologous (dimethylamino)methyl complex $[\{Li(thf)\}_2Cr_2(CH_2NMe_2)_6]$ (188.4(1) pm).[5e] The Cr–Cr bond is bridged by two (dimethylphosphino)methyl ligands in a μ-η^2 fashion. Furthermore, each chromium atom is coordinated by two η^1-CH_2PMe_2 ligands. Because of the molecular symmetry, the ligands exhibit an exactly eclipsed arrangement. The *CrC_3P* unit is far from planar, as the strong deviation from 180° of one of the two angles at Cr between opposite ligands shows (C1-Cr-P1a 177.0(1)°, C2-Cr-C2c 145.2(1)°).

The lithium atoms possess a distorted tetrahedral geometry with the primary donor set defined by two P atoms, one O atom of a THF ligand, and one methylene C atom of the bridging μ-η^2-CH_2PMe_2 ligand. The Li–P bonds are slightly shorter (254.9(4) pm) than those in the six-membered $Li_2C_2P_2$ rings of the dimeric compounds $[\{Li(NN)\}_2(CH_2PRR')_2]$ (**2**) (NN = tmeda, sparteine; R/R′ = Me/Me, Ph/Me, Ph/Ph) (259.3(7)–274(2) pm).[18]

Table 2. Selected structural data of dinuclear alkyl chromate complexes (interatomic distances in pm, angles in °).

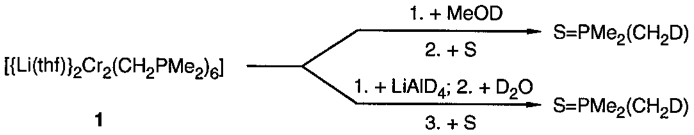
	Bridge type[a]	d(Cr–Cr)	d(Cr–C)	d(Li···C)[b]	d(Li···Cr)[b]	Ref.
$[\{Li(thf)\}_4Cr_2Me_8]$	**I** (4)	198.0(5)	220(1)	237(3)	256(3)	[20]
$[\{Li(ether)\}_4Cr_2(C_4H_8)_4]$[c]	**I** (4)	197.5(5)	216(3)–229(3)	237(7)	254(5)	[21]
$[Cr_2\{(CH_2)_2PMe_2\}_4]$	**II** (4)	189.5(3)	221(1)–223(1)	–	–	[22]
$[\{Li(thf)\}_2Cr_2(CH_2NMe_2)_6]$	**III** (2)	188.4(1)	212.4(4)–213.9(4)	219.7(8)	276.2(6)	[5e]
$[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$ **1**	**IV** (2)	195.0(2)	216.2(3)/220.9(4)	222.6(8)	307.6(6)	[d]
$[\{Li(tmeda)\}_2Cr_2(CH_2PMe_2)_6]$ **1a**	**IV** (2)	194.07(8)	215.1(3)–217.3(3)	293.8(6)	361.4(5)	[d]
$[\{Li_2Cr_2(CH_2PMe_2)_6(tmeda)\}_\infty]$ **1b**	**IV** (2)	193.9(1)	214.5(4)–220.9(4)	222.8(8)	303.1(6)	[d]

[a] Number of bridges in parentheses. [b] Shortest contact is given. [c] C_4H_8 = buta-1,4-diyl. [d] This work.



The Li···C contact mentioned above seems to be relatively strong; this is shown by the Li···C1 distance (226.6(8) pm), which is only slightly longer than those in **2** (212(1)–221(3) pm)[18] and within the range of the Li–C bond lengths in the six-membered $Li_2C_2P_2$ rings (221(1) pm) and the four-membered Li_2C_2 rings (239(1) pm) of the $[\{Li(CH_2PPh_2)(thf)\}_\infty]$ polymeric structure [19] Furthermore, the Li···C distance in **1** is markedly shorter than Li···C distances in other dimeric chromium–alkyl complexes of the $[Li_2Cr_2R_8]$ type (R = Me; R_2 = C_4H_8, butane-1,4-diyl) (237(3), 237(7) pm), but slightly longer than in $[\{Li(thf)\}_2Cr_2(CH_2NMe_2)_6]$ (219.7(8) pm)[5e] (Table 2). The Cr···Li distance (307.6(7) pm) is longer than those in other typical lithium organodichromate(II) complexes.

As expected for a σ-organochromium compound, **1** reacts with MeOD and $LiAlD_4$ to give $PMe_2(CH_2D)$, of which the degree of deuteration (98% and 95%, respectively) was determined by GC–MS after oxidation with sulfur to give $S{=}PMe_2(CH_2D)$ (Scheme 2).



Scheme 2. Reactions of **1** with MeOD and $LiAlD_4$.

The NMR spectra of **1** in solution are consistent with its solid-state structure. The ^{13}C NMR spectrum is shown in Figure 2; the assignment was proved by an NMR attached proton test (APT) experiment and by an H,C-COSY spectrum. Furthermore, it was shown by application of various frequencies (50, 101, 126 MHz) that the signals at δ = 18.0 and 19.8 are two (broadened) singlets and not a doublet or pseudo-doublet. Line broadening due to the residual paramagnetism, and complex spin systems due to the two sets of chemically *and* magnetically nonequivalent ^{31}P nuclei, prevent a more detailed analysis and a simulation of the spectrum.

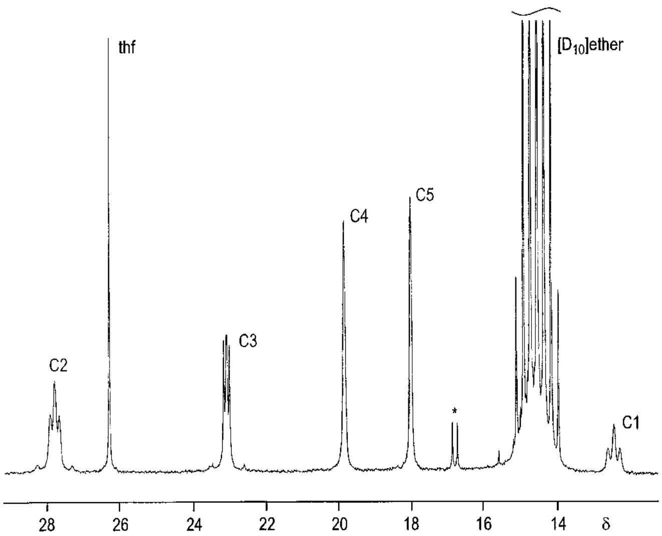


Figure 2. $\{^1H\}^{13}C$ NMR spectrum (101 MHz) of **1** in $[D_{10}]$diethyl ether (THF and diethyl ether signals at δ > 28 are not shown). *Impurity of PMe_3 due to partial hydrolysis.

The ^{31}P NMR spectrum of **1** consists of a broadened singlet (δ = −9.9 in $[D_{10}]$diethyl ether, −12.9 in $[D_6]$benzene) and of a quartet (δ = −52.2 in $[D_{10}]$diethyl ether, −55.2 in $[D_6]$benzene). Compared with uncomplexed PMe_3 (δ = −62)[23] the singlet is strongly shifted to low field. This signal was assigned to the P atom coordinated to chromium; a similar chemical shift ($\delta(^{31}P) = -17.3$) has been observed in $[Cr_2(CH_2SiMe_3)_4(PMe_3)_2]$.[15] The splitting pattern (quartet) of the other signal confirms the coordination of phosphorus to lithium (^7Li 92.6% abundant, $I = 3/2$). The coupling constant, $^1J(^{31}P,^7Li)$ = 60 Hz, is in the expected range for $^1J(^{31}P,^7Li)$ couplings (20–70 Hz).[24] Instead of a quartet, a broadened singlet was observed in THF; this points to dynamic processes with cleavage of the Li–P bonds.

The ^7Li NMR spectrum consists of a broad singlet at δ = 1.48. The half band width ($b_{1/2} \approx 170$ Hz) made it impossible to observe the expected triplet with a line distance of approximately 60 Hz.

Synthesis and characterization of TMEDA adducts of 1: In diethyl ether the addition of tmeda to **1** results in the precipitation of deep red crystals of the TMEDA adducts **1a** and **1b** (Scheme 3).

Complex **1a** is obtained when the crude material is extracted with the mother liquor containing an excess of TMEDA. The adduct **1b** is obtained by recrystallizing the crude material from pure diethyl ether. Recrystallization of **1a** from pure diethyl ether yields **1b** showing that one molecule of TMEDA is readily eliminated from **1a**. Because **1a** and **1b** have a similar appearance, the possibility cannot be excluded that each contains some of the other.

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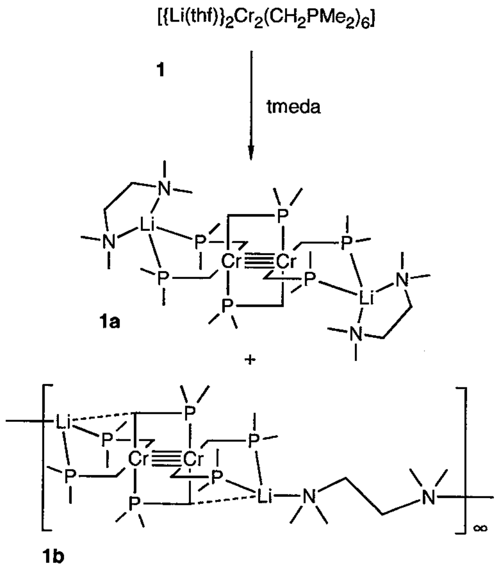

Scheme 3. Synthesis of **1a** and **1b**.

The TMEDA adduct **1a** is pyrophoric and exhibits a relatively high thermal stabiltity (T_{decomp} 140–145 °C). The diamagnetism ($\chi_g = -0.834 \times 10^{-6}$ cm^3 g^{-1}, 295 K) shows that **1a** is a dinuclear chromium complex, too. It reacts with MeOD and vigorously with LiAlD$_4$ to give PMe$_2$(CH$_2$D) (degree of deuteration > 95 %).

The constitution of **1a** and **1b** was confirmed by X-ray structure analyses (Figures 3 and 4; Table 3). Complex **1a** forms discrete molecules. Complex **1b** is a coordination polymer with bridging TMEDA ligands. Both molecules have crystallographically imposed inversion symmetry.

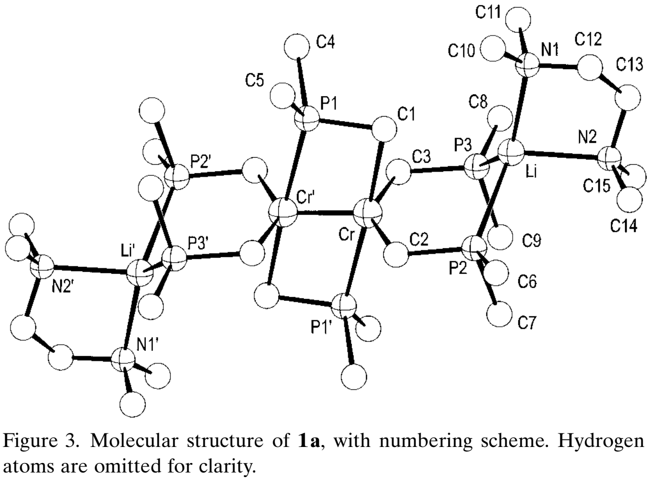

Figure 3. Molecular structure of **1a**, with numbering scheme. Hydrogen atoms are omitted for clarity.

The coordination pattern of the (dimethylphosphino)methyl ligands in **1a** and **1b** is essentially the same as in **1**, but there are remarkable differences in the lithium coordination: in **1a** the primary donor set of the four-coordinate lithium atom is composed of two P atoms and two N atoms of the bidentate TMEDA ligand. In contrast to **1**, there is no Li ··· C1 contact (293.8(6) pm in **1a**, 226.6(8) pm in **1**). Correspondingly, the bending of Li out of the Cr-C2-C3-P2-P3 plane measured by the angles Li-P2-C2 and Li-P3-C3 (111.5(1)°, 110.4(2)°) or by the interplanar angle CrC$_2$P$_2$/P$_2$Li (123.9(1)°) is much larger than those in **1** (Li-P2-C2 96.4(2)°; CrC$_2$P$_2$/P$_2$Li 101.7(2)°). As a consequence the Cr ··· Li separation in **1a** (361.4(5) pm) is much greater than those in **1** (307.6(6) pm), and Cr ··· Li interactions should not play any role.

Table 3. Selected bond lengths [pm] and angles [°] for **1a** and **1b** with standard deviations in parentheses.

	1a	**1b**
Cr–Cr′	194.07(8)	193.9(1)
Cr–P1′	240.11(9)	237.2(1)
Cr–C1	217.3(3)	220.9(4)
Cr–C2	215.1(3)	216.1(4)
Cr–C3	216.0(3)	214.5(4)
P1–C1	178.3(3)	178.3(4)
P2–C2	178.5(3)	178.9(4)
P3–C3	178.6(3)	178.5(4)
Li–P2	259.8(4)	253.3(7)
Li–P3	262.6(5)	252.5(7)
Li–N1	218.3(5)	206.8(7)
Li–N2	223.4(5)	
Li–C1		222.8(8)
C1-Cr-P1′	175.98(9)	176.3(1)
C2-Cr-C3	143.7(1)	144.4(2)
Cr′-Cr-P1′	76.65(3)	76.05(4)
Cr′-Cr-C1	100.17(8)	100.7(1)
Cr-C1-P1	86.1(1)	83.5(2)
Cr-C2-P2	107.8(1)	107.1(2)
Cr-C3-P3	108.1(1)	109.3(2)
Cr′-P1-C1	96.9(1)	99.7(1)
C4-P1-C5	99.5(2)	99.9(3)
Li-P2-C2	111.5(1)	96.7(2)
Li-P3-C3	110.4(2)	95.1(2)
C6-P2-C7	97.1(2)	98.1(3)
C8-P3-C9	97.3(2)	99.1(3)
P2-Li-P3	103.0(2)	109.7(3)
N1-Li-N2	83.3(2)	
N1-Li-C1		113.5(4)

Symmetry transformation (′): $-x, 2-y, 1-z$ (**1a**); $1/2-x, 3/2-y, -z$ (**1b**).

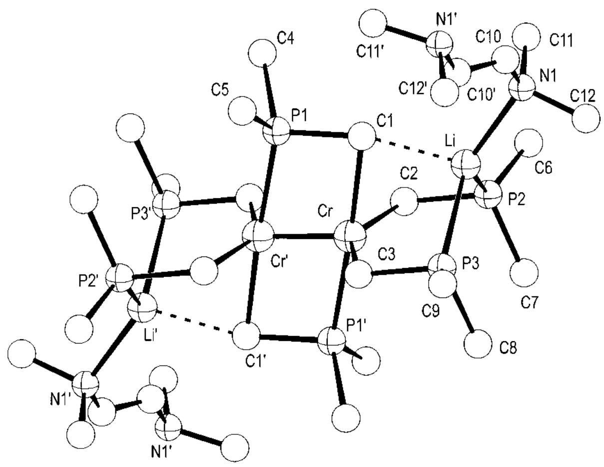

Figure 4. Section of the polymeric structure of **1b**, with numbering scheme. One of the two positions of each of the disordered carbon atoms C10, C11, C12 of the TMEDA ligand is shown. Hydrogen atoms are omitted for clarity.

Apart from the replacement of the THF ligands by monodentate TMEDA ligands, the coordination of lithium in **1** is the same as in **1b**. There are no fundamental differences in the Li ··· C1 distances (222.8(8) pm in **1b**, 226.6(8) pm in **1**), in the Cr⋯Li separation (303.1(6) pm in **1b**, 307.6(6) pm in **1**), and in the bending of Li out of the CrC_2P_2 plane (Li-P2-C2/Li-P3-C3 96.7(2)/95.1(2)° and interplanar angle CrC_2P_2/P_2Li 99.8(2)° in **1b**, Li-P2-C2 96.4(2)° and CrC_2P_2/P_2Li 101.7(2)° in **1**).

Thus, the reactivity of complex **1** to tmeda is different from those of other dinuclear alkyl chromate complexes. Treating a solution of the homologous (dimethylamino)methyl complex $[\{Li(thf)\}_2Cr_2(CH_2NMe_2)_6]$ in THF with tmeda at ambient temperature results neither in substitution of THF nor in any decomposition.[5e] In contrast, treatment of alkyl chromate(II) complexes $[\{Li(thf)\}_4Cr_2R_8]$ (R = Me, CH_2Ph, CH_2CMe_3, CH_2CMe_2Ph) and $[\{Li(thf)\}_2Cr_2(CH_2SiMe_3)_6]$ with tmeda results in the cleavage of the Cr–Cr bonds. From this, the existence of Cr–Cr bonds in these complexes has been questioned.[25]

In all three complexes **1**, **1a**, and **1b** the Cr–Cr quadruple bond is supported by two-atom bridging ligands (μ-η^2-CH_2PMe_2) forming four-membered rings Cr_2CP (see bridge type **IV**, Table 2). In marked contrast, the analogous (amino)methyl complex $[\{Li(thf)\}_2Cr_2(CH_2NMe_2)_6]$ forms seven-membered rings $Cr_2CNLiNC$ (see bridge type **III**, Table 2).[5e] This difference may be explained in terms of the larger covalent radius of phosphorus and the higher angular flexibility in phosphanes.

Cr–Cr quadruple bonds bridged in such a way that four-membered rings (Cr_2CP) are formed had never previously been observed. Five-membered rings (for example, Cr_2OCO in $[Cr_2(O_2CR)_4]$, Cr_2CPC in $[Cr_2\{(CH_2)_2PR_2\}_4]$, Cr_2CCO in $[Cr_2\{C_6H_4(o\text{-}OR)\}_4]$[17]) are predominant. But three- (Cr_2C in $[Cr_2(CH_2SiMe_3)_4(PMe_3)_2]$,[26] $[\{Li(thf)_2\}_2Cr_2(CH_2SiMe_3)_6]$[25c]), six- ($Cr_2CCCN$ in $[Cr_2\{CH_2C_6H_4(o\text{-}NMe_2)\}_2(O_2CMe)_2]$[27]), and seven-membered rings (see above) are also known.

The dinuclear chromium complex **1** is the first homoleptic (phosphino)methyl transition metal complex. Its reaction with tmeda giving the TMEDA adducts **1a** and **1b** without cleavage of the Cr–Cr bond is of special interest with respect to the reactivity and strength of Cr–Cr quadruple bonds.

Experimental Section

All reactions and manipulations were carried out under purified argon using Schlenk techniques. Diethyl ether and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl under argon; pentane, hexane, and tmeda were distilled from $LiAlH_4$ under argon. NMR spectra were recorded on Varian spectrometers (Unity 500, Gemini 2000, Gemini 200) using the protio impurities and the ^{13}C resonances of the deuterated solvents as references for ^1H and ^{13}C NMR spectroscopy, respectively. The chemical shifts $\delta(^{31}P)$ and $\delta(^7Li)$ are reported relative to H_3PO_4 (85 %) and a saturated solution of LiCl in $[D_8]$THF (external). The chromium contents were determined by ICP atomic emission spectroscopy (PU 7000, Unicam). Room-temperature magnetic susceptibilities were determined with a home-made balance by the Gouy method. GC–MS investigations were carried out on HP5890 Series II/HP5972 (Hewlett Packard) instruments. $[CrCl_2(thf)_2]$ was obtained by extraction of $CrCl_2$ with THF.[28] $LiCH_2PMe_2$ was prepared by metalating PMe_3 with *tert*-butyllithium in pentane/hexane.[14]

Synthesis of $[\{Li(thf)\}_2Cr_2(CH_2PMe_2)_6]$ (1): $[CrCl_2(thf)_2]$ (2.68 g, 10.0 mmol) was added gradually to a solution of $LiCH_2PMe_2$ (3.28 g, 40.0 mmol) in diethyl ether (60 mL) at −50 °C and the solution turned red. The mixture was allowed to warm to room temperature, the colorless precipitate of LiCl was filtered off and THF (2–3 mL) was added. The red precipitate of **1** was recrystallized from diethyl ether. Yield 2.85 g (80 %); ^1H NMR (200 MHz, $[D_{10}]$diethyl ether): $\delta = -0.65$ ('t', 4H; $2C^1H_2$), 0.61 ('s', 20H; $4C^2H_2$ and $4C^4H_3$ or $4C^5H_3$), 0.95 ('s', 12H; $4C^3H_3$), 1.44 ('t', 12H, $4C^4H_3$ or $4C^5H_3$), 1.79 (m, 8H; THF), 3.65 (m, 8H; THF); ^{13}C NMR (101 MHz, $[D_{10}]$diethyl ether): $\delta = 12.4$ ('t'; CH_2), 18.0 ('s'; CH_3), 19.8 ('s'; CH_3), 23.0 ('q'; CH_3), 27.7 ('t'; CH_2); ^{31}P NMR (202 MHz, $[D_6]$benzene): $\delta = -12.9$ (s), −55.2 (q, $^1J(P,Li) = 60$ Hz); ^7Li (195 MHz, $[D_{10}]$diethyl ether): $\delta = 1.48$ (br s); $C_{26}H_{64}Cr_2Li_2O_2P_6$ (712.51): calcd.: Cr 14.60; found: Cr 14.30.

Synthesis of 1a and 1b: tmeda (0.5 mL, 4.4 mmol) was added to a solution of **1** (0.50 g, 0.7 mmol) in diethyl ether (25 mL). The solution became colorless and red crystals of **1a** and **1b** were precipitated. The precipitate was filtered and dried in vacuo. Yield 0.52 g.

Crystals suitable for X-ray investigations were obtained by extracting the product with the mother liquor (diethyl ether/tmeda) (**1a**) and pure diethyl ether (**1b**), respectively.

1a: $T_{decomp} = 140-145$ °C; ^{31}P NMR (81 MHz, $[D_{10}]$diethyl ether): $\delta = -6.3$ (s), −46.0 (q, $^1J(P,Li) = 62$ Hz).

Reactions of 1 and 1a with MeOD and $LiAlD_4$:

MeOD: MeOD (2 mL) was added at −20 °C to the complex (ca. 100 mg) in diethyl ether (10 mL). The mixture was stirred at room temperature overnight, the precipitate was filtered off and sulfur (ca. 200 mg) was added. The degree of deuteration of $S{=}PMe_2(CH_2D)$ was determined by GC–MS.

$LiAlD_4$: $LiAlD_4$ (100 mg) was slowly added at −50 °C to the complex (ca. 200 mg) in diethyl ether (10 mL). The mixture was allowed to warm to room temperature within 1 h and stirred for 1 h at room temperature. The excess of $LiAlD_4$ was decomposed with D_2O at −70 °C. After addition of sulfur the ethereal phase was analyzed by GC–MS.

X-ray crystallography: Suitable single crystals (**1**: red, prismatic; **1a**: red, rod-shaped; **1b**: red, rhombic) were mounted quickly on a glass fiber using perfluoroether under a cold stream of N_2. X-ray measurements were performed on a Nicolet R3/mV (**1**), STOE-IPDS (**1a**), and Siemens P4 diffractometer (**1b**) at 170 K (**1**), 220 K (**1a**), and 200 K (**1b**), respectively. Intensities were collected with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda_0 = 0.71073$ Å). Absorption corrections for **1** and **1b** were carried out semiempirically by ω scans and numerically for **1a**. The structures were solved by direct methods with SHELXS-86[29] and refined by using full-matrix least-squares procedures on F^2 (SHELXL-93).[30] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included with isotropic thermal parameters of 1.2 times the equivalent isotropic thermal parameters of the corresponding carbon atoms. The carbon atoms (C10, C11, C12) of the TMEDA ligand in complex **1b** are disordered and occupy two positions with the same probability. A summary of crystallographic data, details of data collection, structure solution, and refinement is given in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101390. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk). Figures were drawn with the Diamond program.[31]

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Table 4. Summary of crystal data, details of data collection, structure solution, and refinement for **1**, **1a**, and **1b**.

	1	**1a**	**1b**
empirical formula	$C_{26}H_{64}Cr_2Li_2O_2P_6$	$C_{30}H_{80}Cr_2Li_2N_4P_6$	$C_{24}H_{64}Cr_2Li_2N_2P_6$
fw	712.47	800.68	684.47
crystal size [mm]	0.60 × 0.50 × 0.50	0.40 × 0.20 × 0.10	0.40 × 0.40 × 0.30
crystal system/space group	monoclinic/$I2/m$ (no 12)	monoclinic/$P2_1/n$ (no 14)	monoclinic/$C2/c$ (no 15)
a [pm]	1170.2(7)	1059.7(2)	1658.1(5)
b [pm]	1248.0(9)	1939.7(4)	1238.7(4)
c [pm]	1380.9(5)	1164.0(3)	1882.7(6)
β [°]	92.69(3)	94.43(2)	94.03(2)
Z	2	2	4
V [nm^3]	2.014(2)	2.3857(9)	3.857(2)
ρ_{calcd} [g cm^{-3}]	1.175	1.115	1.179
μ [mm^{-1}]	0.797	0.679	0.827
θ range [°]	2.2–25.0	2.2–25.0	2.1–25.0
T_{min}/T_{max}	0.671/0.946		
reflections collected	3993	16868	3535
independent reflections	1849 ($R_{int} = 0.0645$)	4197 ($R_{int} = 0.0978$)	3409 ($R_{int} = 0.0282$)
observed refl. [$F_o \geqslant 4\sigma(F_o)$]	1847	3107	2469
data/restraints/parameters	1568/0/102	4197/0/269	3409/0/286
goodness-of-fit on F^2	1.061	0.969	0.972
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0408$, $wR2 = 0.1042$	$R1 = 0.0382$, $wR2 = 0.0893$	$R1 = 0.0519$, $wR2 = 0.1239$
R indices (all data)	$R1 = 0.0493$, $wR2 = 0.1134$	$R1 = 0.0580$, $wR2 = 0.0966$	$R1 = 0.0721$, $wR2 = 0.1313$
larg. diff. peak/hole [e nm^{-3}]	461/ – 365	678/ – 272	574/ – 1233

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