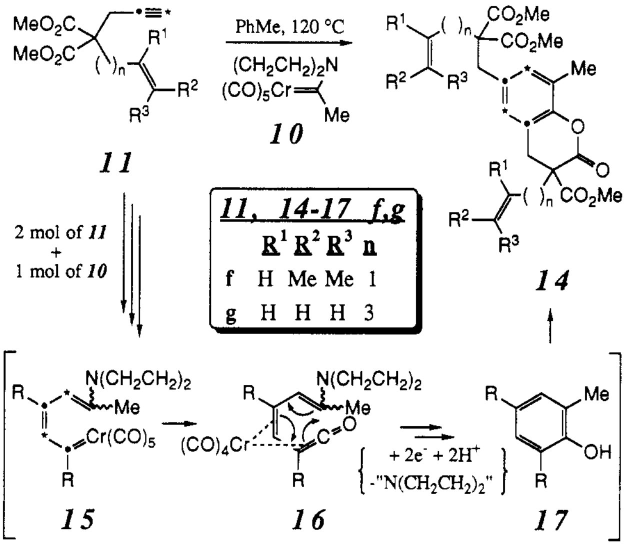
for the vinyl (**11a**), methallyl (**11b**), and (*E*)- and (*Z*)-crotyl (**11d** and **11c**) systems. This is in significant contrast to the case of the methoxy-bearing carbene **1**.[2] The fused bicyclo[4.1.0]heptane **12e**, whose formation is presumably slowed by virtue of generation of a six- rather than five-membered ring, was also formed in better yield with **10** than **1**.

The increased electron-donating ability of the pyrrolidino compared to the methoxy substituent results in the necessity for higher temperatures to achieve comparable reaction rates (~120 °C vs ~80 °C), consistent with a slower initial dissociation of carbon monoxide to a 16-electron chromium species capable of initiating reaction with the alkyne. Moreover, the amino group expresses its donor power again at the stage of the vinylogous donor-stablized carbene complex **7** ($X = NR_2$) by slowing the rate of carbon monoxide insertion and ketene formation. However, we did eventually see products derived from carbon monoxide incorporation in reactions of **10**. The substrates **11f** and **11g** which contain additional hindrance on the alkene and a longer tether, respectively, apparently undergo cyclopropanation more slowly than any of **11a**–**e**. The only identifiable products from their reaction with **10** were the aromatic lactones **14f** and **14g** in 48% and 59% yields, respectively. These 2:1 adducts can arise via the butadienylogous aminocarbenes **15** (formed by addition of the vinylogous carbene **7** to a second molecule of enyne **2**) in which the donating capability of the pyrrolidino group to the metal center is diminished to the point where CO insertion becomes kinetically viable. The resulting ketene complexes **16** can undergo reductive cyclization to the two-alkyne phenols **17**, precursors to the lactones **14**, by a precedented redox process.[8]



We believe that other applications[9] which demonstrate the advantageous behavior of amino-substituted Fischer carbene complexes will continue to surface. This work simultaneously demonstrates that amino substituents can alter the reactivity patterns of these species in synthetically profitable ways and provides new insight to the mechanism of this important class of organometallic reagents.

Acknowledgment. This investigation was supported by Grant GM-38854 awarded by the DHHS and by an award from the Alfred P. Sloan Foundation.

Supplementary Material Available: Spectral and characterization data for compounds **12a**, **12b**, **12c**, **12d**, **12e**, **14f**, **14g**, and **ii** (5 pages). Ordering information is given on any current masthead page.

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Deprotonation of Bis(dimethylphosphino)ethane Ligand of a Cationic Chromium Alkyl

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Summary: Reaction of cationic chromium alkyl $[Cp^*Cr(dmpe)CH_3]^+PF_6^-$ with strong base proceeded via deprotonation of a methyl group of coordinated bis(dimethylphosphino)ethane and yielded a complex containing a six-membered $\overline{\text{CrCPCCP}}$ heterocycle. The crystal structure of this compound was determined, and its isomerization and reactions with electrophiles were investigated.

As part of our study of the reactivity of paramagnetic organometallics we have recently described some cationic chromium(III) alkyl complexes of the type $[Cp^*Cr(L)_2R]^+X^-$.[1] These complexes catalyze the polymerization of ethylene and serve as homogeneous models for commercially used heterogeneous catalysts based on chromium.[2] It has been noted that olefin polymerization catalysts are closely related chemically to catalysts for the olefin metathesis reaction.[3] The latter reaction has generated some excitement as of late in the form of the ring opening metathesis polymerization (ROMP) of cyclic olefins.[4] We reasoned that deprotonation of a cationic chromium alkyl[5] might yield an alkylidene, which could initiate olefin metathesis.[6] Herein we report an unexpected result of this approach.

Addition of 1.0 equiv of the base $LiN(SiMe_3)_2$ to a THF solution of $[Cp^*Cr(dmpe)Me]^+PF_6^-$ (**1**) resulted in an im-

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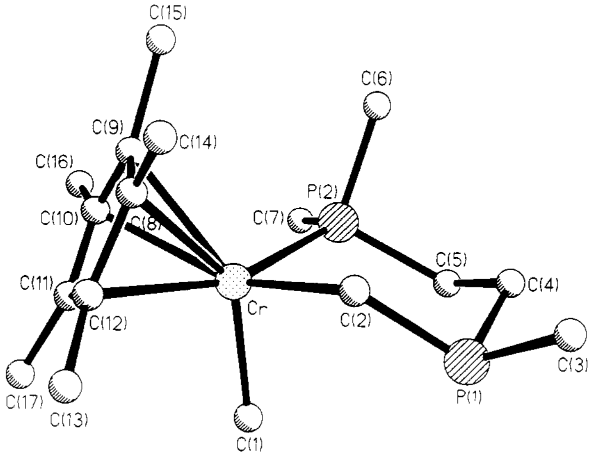
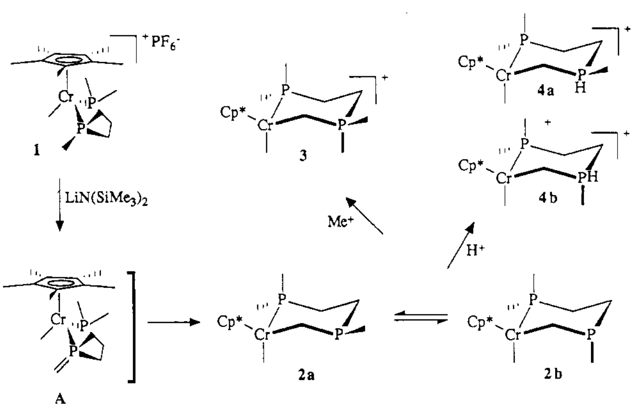


Figure 1. The molecular structure of **2a**. Selected bond distances: Cr–C1, 2.067 (11) Å; Cr–C2, 2.094 (9) Å; Cr–P2, 2.402 (3) Å; P1–C2, 1.806 (9) Å. Interatomic angles: C1–Cr–C2, 96.6 (4)°; C2–Cr–P2, 89.6 (3)°; C1–Cr–P2, 91.6 (3)°; Cr–C2–P1, 119.8 (5)°; C2–P1–C3, 103.6 (5)°; C2–P1–C4, 103.7 (4)°.

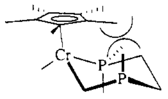
Scheme I



mediate color change of the solution from red to purple. Evaporation of solvent and extraction of the solid residue with pentane followed by recrystallization from the same solvent at −30 °C yielded crystals of a new compound (**2**) in 65% yield. The mass spectrum of this material exhibited a peak at m/e = 351, consistent with the molecular ion of the desired alkylidene, and the elemental analysis also fit that chemical constitution.[7] However, the ^{1}H NMR spectrum of **2**—despite being broadened and shifted severely due to its paramagnetic nature—exhibited too many resonances to account for. In addition, the reactivity of the new compound was not that expected of the sought methylene complex. For example, reprotonation of **2** with strong or weak acid (HBF$_4$ or NH$_4$PF$_6$, respectively) led to yet another new compound (see below) rather than regenerating **1**. The mystery was finally solved by an X-ray structure determination.

The structure of **2** is shown in Figure 1.[8] The complex features an unusual six-membered heterocycle, which adopts a chair conformation. The chromium-bound methyl group remains intact and is joined by a second alkyl ligand derived from one of the methyl groups of the chelating phosphine. The pentamethylcyclopentadienyl ring and the unadulterated phosphine terminus of the dmpe ligand complete the coordination sphere of chromium in the familiar geometry of a three-legged piano stool. The chromium–carbon bond distances of 2.067 (11) Å (Cr–C1) and 2.094 (9) Å (Cr–C2) are similar to those in related chromium(III) alkyls structurally characterized by others and us.[9] The chromium–phosphorus bond distance of 2.402 (3) Å is unusually large by comparison with other dmpe complexes of chromium[10] and vis à vis the sum of the covalent radii (2.24 Å). It is also substantially longer than the corresponding distances in the closely related compound Cp*Cr^{II}(dmpe)CH$_3$ (Cr–P = 2.30 Å).[11] We believe the latter difference must reflect the decreasing contribution of π-back-bonding to the phosphine upon raising the formal oxidation state from +II to +III. **2** apparently resulted from deprotonation of a methyl group of the coordinated bis(dimethylphosphino)ethane[12] and subsequent rearrangement of the intermediate ylide (A in Scheme I). While the C–H acidity of bis(dimethylphosphino)ethane must be very low, coordination to the highly electrophilic chromium center in cationic **1** greatly facilitated its deprotonation.

A fresh solution of **2** in benzene-d_6 exhibited broadened signals attributable to one Cp* ligand (21.2 ppm) and three inequivalent methyl groups (−6.0, −21.0, and −31.8 ppm). However, upon standing at room temperature for several hours a second set of resonances with the same ratio of intensities had grown in (23.4, −16.4, −23.0, −46.1 ppm), eventually reaching an equilibrium ratio of ca. 2:1. We interpret these observations as a reversible isomerization by pyramidal inversion[13] of the uncoordinated phosphine moiety, thus converting the crystallography characterized **2a** with an equatorial methyl group (see Scheme I) into the slightly less stable isomer **2b** with an axial methyl substituent. An alternative assignment of the second isomer as resulting from a ring flip is untenable because such a rearrangement would put the extremely bulky Cp* group in an axial position and force it into a severe 1,3-diaxial interaction with the methyl group on the uncoordinated phosphorus (structure B). In addition, the ring flip should be fast on the ^{1}H NMR time scale[14] and hence not lead to the observation of the two isomers by this spectroscopic technique. We were somewhat surprised by the apparent ease of the isomerization, however. The half-life of the equilibration (ca. 4.3 h) allowed an estimation of the free energy of activation of $\Delta G^{\ddagger}$ = 24 kcal/mol. This barrier was substantially lower than values measured for simple organic phosphorinanes ($\Delta G^{\ddagger}$ = 35 kcal/mol).[15] A possible explanation for this discrepancy may lie in a significant stabilization of the planar transition state of the inversion by a π-interaction of the phosphorus



B

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[7] **2**: ^{1}H NMR (C$_6$D$_6$) **2a** 21.2 (15 H), −6.0 (3 H), −21.0 (3 H), −31.8 ppm (3 H); **2b**, 23.4 (15 H), −16.4 (3 H), −23.0 (3 H), −46.1 (3 H); **2a**/**2b** = 2.0; methylene protons and protons of chromium-bound methyl group were not observed. IR (KBr): 2940 (s), 2894 (s), 2856 (s), 2728 (w), 1458 (w), 1417 (s), 1376 (s), 1283 (m), 980 (m), 944 (vs), 707 (s), 681 (m), 634 (m), 579 (m), 545 (m) cm^{-1}. Mp: 114–115 °C. Anal. Calcd for C$_{17}$H$_{33}$P$_2$Cr: C, 58.11; H, 9.47. Found: C, 57.84; H, 9.70.

[8] Purple cubes from pentane; monoclinic $C2/c$; a = 29.21 (2) Å, b = 8.187 (4) Å, c = 16.934 (6) Å, β = 96.17 (4)°; Z = 8; R = 0.084, R_w = 0.123.

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lone pair with a half-filled d orbital on chromium.

The free phosphine moiety made **2** susceptible to electrophilic attack. Reaction with $Me_3O^+BF_4^-$, for example, yielded the phosphonium salt **3**.[16] As expected, ^1H NMR resonances for only one isomer of **3** were observed. This compound may also be viewed as an ylide complex[17] and is closely related to Werner's structurally characterized $Cp(I)\overline{RhCH_2P(CH_3)_2CH_2CH_2P}(CH_3)_2$,[18] which was shown to adopt a chair configuration very similar to that of **2**. In addition several chromium compounds reported by Weber et al. serve as precedent for this unusual six-membered heterocycle.[19] Protonation of **2** did not regenerate **1** but rather yielded a mixture of compounds (ca. 2:1 ratio) to which we tentatively assign the structures **4a**,**b** (Scheme I).[20]

We conclude that the C–H bonds of ligands in cationic chromium(III) complexes are strongly activated with respect to deprotonation. Judicious choice of deprotonation resistant supporting ligands should ultimately lead to proton abstraction from alkyl ligands, thus generating chromium(III) alkylidenes. Efforts to isolate and characterize such compounds are currently underway in our laboratory.

Acknowledgment. This research was supported by the National Science Foundation (CHE-8512710).

Supplementary Material Available: Tables of crystal data and summary of data collection and refinement, fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for **2** (8 pages). Ordering information is given on any current masthead page.

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[16] **3**: ^1H NMR (CD_2Cl_2) 43.9 (1 or 2 H), 22.5 (1 or 2 H), 10.7 (3 H), 8.0 (15 H), −4.7 (3 H), −14.3 (3 H), −34.5 ppm (3 H); IR (KBr) 2960 (m), 2914 (s), 2894 (m), 1424 (m), 1379 (m), 1298 (m), 1057 (vs), 960 (s), 892 (m), 818 (w), 730 (w), 520 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{36}BCrF_4P_2$: C, 47.70; H, 8.01. Found: C, 47.67; H, 8.20.

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[20] **4**: ^1H NMR (CD_2Cl_2) **4a**, 8.6 (15 H), 0.1 (3 H), −15.7 (3 H), −30.3 ppm (3 H); **4b**, 6.7 (15 H), −6.2 (3 H), −25.8 (3 H), −37.3 (3 H). IR (KBr): 2922 (m), 2914 (m), 1486 (w), 1420 (s), 1410 (m), 1300 (m), 1058 (vs), 952 (s), 894 (s), 842 (w), 740 (w), 520 (m), 427 (w) cm^{-1}. FAB-MS: *m/e* 352. Several attempts to obtain an elemental analysis of **4** gave erratic results. Deprotonation of **4** with $LiN(SiMe_3)_2$ regenerated **2**.

Facile Olefin Hydrogenation with an Osmium Dihydrogen Complex

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Summary: The cation $OsH_5P_3^+$ (P = PMe_2Ph) is shown to contain and reversibly dissociate H_2 and to hydrogenate ethylene and 1,5-cyclooctadiene with production of $OsH(C_2H_4)_2P_3^+$ and $OsH(COD)P_3^+$. The structure of the ethylene complex is analyzed by extended Hückel methods. $OsH_5P_3^+$ catalytically hydrogenates cyclohexene.

We have shown,[1] before the demonstration that H_2 can exist intact as a ligand,[2] that the tetrahydride[3] OsH_4P_3 (P = PMe_2Ph) can be protonated to $OsH_5P_3^+$. Success in working with this cation is critically dependent on employing a "noncoordinating" solvent (e.g., CH_2Cl_2) and a "nonnucleophilic" partner for the acid (e.g., $HBF_4{\cdot}OEt_2$). We now report new observations concerning this polyhydride cation.

The cation $OsH_5P_3^+$ is a fluxional species that shows (360-MHz ^1H or 146-MHz ^{31}P NMR) a single $H_5(Os)$ and a single phosphorus resonance down to −85 °C. The T_1 values of OsH_4P_3 and $OsH_5P_3^+$ are 270 and 68 ms, respectively, at 360 MHz and −70 °C in toluene-d_8 and CD_2Cl_2, consistent with[4] the presence of one (or more) H_2 ligands in the cation. If this H_2 ligand is reversibly dissociated (eq 1),[5,6] this serves as a mechanism for the rapid

$$OsH_5P_3^+ \rightleftarrows H_2 + OsH_3P_3^+ \qquad (1)$$

deuteration of the hydride ligands observed when $OsH_5P_3^+$ is treated with D_2 at 25 °C. More important, eq 1 furnishes a *rare*[7,8] example of a 16-valence electron polyhydride complex. The observation that $OsD_5P_3^+$,[9] in CH_2Cl_2 solution over 10 h, shows deuteration of the ortho phenyl sites, is an indication of the high reactivity (i.e., ortho metalation) of $OsD_3P_3^+$.[10]

Ethylene (1 atm) reacts at 25 °C with $OsH_5P_3^+$ to give ethane and *cis,mer*-$OsH(C_2H_4)_2P_3^+$.[11] No H_2 is observed (^1H NMR). Both olefins rotate rapidly at 25 °C in this stereochemically rigid octahedron, but the olefins show no mutual site exchange on the NMR time scale. Olefin rotation is slowed by −40 °C, but the number (four) of ethylene proton resonances fails to uniquely establish the ground-state orientation of the ethylene C═C vectors. The crystal structure[12] (Figure 1) shows that the C═C vectors (1) eclipse the Os–ligand directions, (2) are mutually orthogonal, and (3) leave the Os—H and one C═C bond coplanar (i.e., in a geometry suited to β-hydrogen migration). In spite of this third point, the long (2.26 (7) Å) H1–C3 distance excludes an agostic ethyl ground-state geometry.

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[5] This preequilibrium was also established by a kinetic study[1] of the conversion of $OsH_5P_3^+ + MeCN \rightarrow OsH_3(MeCN)P_3^+ + H_2$.

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[9] D_4OsP_3, from $LiAlD_4$, shows no deuterium scrambling to ortho phenyl positions. This compound was then treated with $DBF_4{\cdot}OMe_2$.

[10] Ortho metalation of PMe_2Ph is rare and is a much more stringent test of reactivity than ortho metalation of PPh_3. See: Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39.

[11] Spectral data for $OsH(C_2H_4)_2P_3^+$: ^1H NMR (360 MHz, 24 °C, CD_2Cl_2): δ −6.77 (dt, $J(PH) = 30, 21$ Hz, 1 H), 1.32 (d, $J(PMe) = 8$ Hz, 6 H), 1.40 (br s, C_2H_4 cis to H, 4 H), 1.47 (vt, 3 Hz, 6 H), 1.61 (vt, 3 Hz, 6 H), 2.94 (dt, C_2H_4 trans to H, $J(C_2H_4{-}P) = J(C_2H_4{-}H) = 3$ Hz, 4 H), 7.30 (m, PPh). $^{13}C\{^1H\}$ NMR of the ethylene carbons: δ 40.28 (d, $J(C{-}P) = 11$ Hz), 40.83 (s). $^{31}P\{^1H\}$ (146 MHz, 24 °C, CD_2Cl_2): $\delta = -41.5$ (t, $J(P{-}P) = 14$ Hz, 1 P), −36.5 (d, $J(P{-}P) = 14$ Hz, 2 P).

[12] Crystallographic data for $[OsH(C_2H_4)_2(PMe_2Ph)_3]BF_4{\cdot}CH_2Cl_2$ at −155 °C: $a = 13.134$ (7) Å, $b = 13.300$ (8) Å, $c = 11.011$ (7) Å, $\alpha = 111.25$ (2)°, $\beta = 113.15$ (3)°, $\gamma = 89.26$ (3), $Z = 2$ in $P\bar{1}$. $R(F) = 0.0280$ for 4050 reflections with $F > 2.33\sigma$ refining all atoms including hydrogens.

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