J. Am. Chem. Soc. 1987, 109, 5693–5698 5693

the π/π^* frontier molecular orbital interaction (vs. σ/π^*) leads to a [2 + 2] cycloaddition reaction (nonconcerted) product. Theoretical calculations[12] support this conclusion.

Experimental Section

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 467 spectrometer. Field desorption mass spectra were obtained on a Finnigan MAT 311A mass spectrometer. All ^{1}H NMR spectra were obtained on a Bruker WH-200 instrument, and the chemical shifts are reported in ppm from internal TMS.

The proton-decoupled ^{31}P spectra were acquired on a Bruker HX90E/SXP spectrometer using the standard multinuclear probe head. Samples were run with $CDCl_3$ as solvent in 10-mm tubes. Chemical shifts were measured relative to an external capillary of 85% aqueous H_3PO_4. Typical conditions: recycle time, 10 s; 90° rf pulse width, 15 μs; spectral width, 12048 Hz in 8192 points.

Crystals suitable for the X-ray structure were made by recrystallizing **3** from chloroform. The X-ray intensity data (11369 reflections, $2.0° \leq 2\theta \leq 50.0°$, $h,\pm k,\pm l$, 2θ scan) from a single crystal of **3** were recorded on a Syntex P2 four-circle diffractometer at ambient temperature using graphite-monochromated Mo Kα radiation. The 2780 reflections with $I > 3.0\sigma(I)$ were corrected for Lorentz, decay, and polarization effects. The initial P and O atom positions were located with MULTAN. All remaining non-hydrogen atom positions were located by subsequent difference Fourier techniques. All computations were made with the UCLA Crystallographic Package installed on a DEC VAX 8600/750 cluster.

Preparation of 3. **1a** (10 g, 12.5 mmol) is sublimed at 220 °C (1–1.2 kPa) for 4 h. The sublimate (~6 g) is then stirred in diethyl ether (25–30 mL) for 20 min to extract **1a**. Filtration affords 3.2 g (32%) of nearly pure[3] product: mp 174–182 °C; IR (Nujol) 1175, 1100, 888, 870, 853 (P–O–P), 772, 755, 730, 720, and 700 cm^{-1}; field desorption/mass spectrometry (FD/MS) m/e 532 (trace of m/e 266); ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 36 H), 2.30 (s, 6 H), 7.14 (s, 4 H); ^{31}P{^{1}H} NMR ($CDCl_3$) 176.5 ppm.

NMR Study. **4** (0.5 g, 1.6 mmol) is placed in a 10-mm NMR tube and dissolved in THF. Sufficient $CDCl_3$ is added for a lock signal. TEA (0.32 g, 3.2 mmol) is added and the spectrum is taken. Then water (0.028 g, 1.6 mmol, 28 μL) is added in 7-μL increments with a microliter syringe. After each addition, the spectrum is run.

Acknowledgment. We thank Perry Matheny for his synthetic assistance and Barbara Bancroft of Texas A&M University for performing the molecular orbital calculations.

Supplementary Material Available: Tables S1, S2, and S3 listing hydrogen atomic parameters, anisotropic thermal parameters, and isotropic thermal parameters (4 pages); table of observed and calculated structure factor amplitudes for **3** (13 pages). Ordering information is given on any current masthead page.

---

[12] Bancroft, B., private communication, Mar 1986.

Reaction of Bulky Monosubstituted Phosphorus(III) Halides with Disodium Pentacarbonylchromate. Steric and Electronic Factors in the Synthesis of $Cr(CO)_5$ Complexes of Diphosphenes, Phosphinidenes, Phosphanes, Diphosphanes, and Cyclopolyphosphanes

Ruth A. Bartlett, H. V. Rasika Dias, Kathy M. Flynn, Hakon Hope, Brendan D. Murray,[1] Marilyn M. Olmstead, and Philip P. Power*[2]

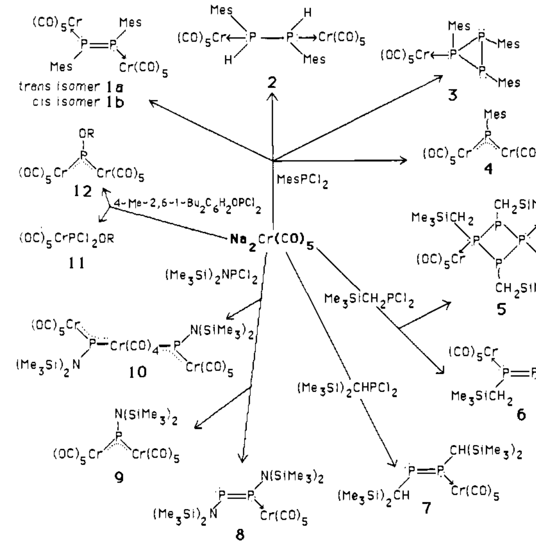
Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received December 24, 1986*

Abstract: Reaction of $Na_2Cr(CO)_5$ with a bulky monosubstituted phosphorus(III) halide, $RPCl_2$, where R = 2,4,6-$Me_3C_6H_2$ (Mes), CH_2SiMe_3, $CH(SiMe_3)_2$, $N(SiMe_3)_2$, or –OC_6H_2-2,6-*t*-Bu_2-4-Me, leads to at least nine different types of product which may involve diphosphene, phosphinidene, phosphane, diphosphane, and cyclopolyphosphane ligands. The products obtained depend markedly on the size and electronic properties of the substituent on phosphorus. The synthesis and properties of 12 compounds of which 10 have been structurally characterized by X-ray crystallography are described in this paper. IR and ^{31}P NMR data are also reported. The compounds are [*trans*-$(PMes)_2\{Cr(CO)_5\}_2$] (**1a**), [$\{Cr(CO)_5\}_2\{P(H)Mes\}_2$] (**2**), [$Cr(CO)_5\{$*cyclo*-$(PMes)_3\}$] (**3**), [$\{Cr(CO)_5\}_2\{$*cyclo*-$(PCH_2SiMe_3)_4\}$] (**5**), [*trans*-$(PCH_2SiMe_3)_2\{Cr(CO)_5\}_2$] (**6**), [*trans*-$\{PCH(SiMe_3)_2\}_2Cr(CO)_5$] (**7**), [*trans*-$\{PN(SiMe_3)_2\}_2Cr(CO)_5$] (**8**), [$\{Cr(CO)_5\}_2PN(SiMe_3)_2$] (**9**), [*trans*-$\{Cr(CO)_4\}\{PN(SiMe_3)_2Cr(CO)_5\}_2$] (**10**), [$Cr(CO)_5(PCl_2OC_6H_2$-2,6-*t*-$Bu_2$-4-Me)] (**11**), and [$\{Cr(CO)_5\}_2(POC_6H_2$-2,6-*t*-$Bu_2$-6-Me)] (**12**). Details of the structures of complexes **1a**, **2**, **3**, **5**, and **6** in addition to **11** and **12** are described and discussed in conjunction with those of **7**, **9**, and **10** which have been reported in preliminary publications. Crystal data [Mo Kα (λ = 0.71069 Å)] at 130 K are as follows: **1a**, $C_{28}H_{22}Cr_2P_2O_{10}$, a = 11.170 (6) Å, b = 16.159 (8) Å, c = 9.260 (5) Å, β = 113.91 (4)°, Z = 2, monoclinic, space group $P2_1/c$, R = 0.0745; **2**, $C_{28}H_{22}Cr_2P_2O_{10}\cdot C_6H_{14}$, a = 9.008 (4) Å, b = 9.418 (4) Å, c = 11.625 (3) Å, α = 96.77 (3)°, β = 112.21 (3)°, γ = 94.69 (4)°, Z = 1, triclinic, space group $P\bar{1}$, R = 0.052; **3**, $C_{32}H_{33}CrP_3O_5$, a = 10.507 (6) Å, b = 11.437 (7) Å, c = 14.707 (9) Å, α = 110.95 (4)°, β = 90.49 (5)°, γ = 104.48 (4)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.045; **5**, $C_{26}H_{44}Cr_2P_4O_{10}Si_4$, a = 10.322 (4) Å, b = 19.180 (4) Å, c = 11.198 (4) Å, β = 109.79 (2)°, Z = 2, monoclinic, space group $P2_1/c$, R = 0.050; **6**, $C_{18}H_{22}Cr_2P_2O_{10}Si_2$, a = 6.989 (3) Å, b = 9.226 (4) Å, c = 10.975 (5) Å, α = 106.08 (3)°, β = 93.36 (3)°, γ = 94.58 (3)°, Z = 1, triclinic, space group $P\bar{1}$, R = 0.064; **11**, $C_{20}H_{23}CrPO_6Cl_2$, a = 13.068 (2) Å, b = 11.426 (3) Å, c = 15.852 (4) Å, β = 93.81 (2)°, Z = 4, monoclinic, space group $P2_1/a$, R = 0.031; **12**, $C_{25}H_{23}Cr_2PO_{11}$ (at 293 K), a = 9.224 (1) Å, b = 16.549 (2) Å, c = 20.240 (2) Å, α = 73.74 (1)°, β = 80.44 (1)°, γ = 87.50 (1)°, Z = 4 (2 dimers), triclinic, space group $P\bar{1}$, R = 0.056.

Compounds that contain unsupported double bonds between heavier main group elements have been made accessible primarily through the use of bulky substituents[3-5] which ensure kinetic stabilization by preventing association and further reaction of the

0002-7863/87/1509-5693$01.50/0 © 1987 American Chemical Society

Scheme I. Summary of the Products Derived from the Reaction of $Na_2Cr(CO)_5$ with Various Monosubstituted Phosphorus(III) Halides



double bonded species. Heavier main group IV multiple bonds in molecules such as R_2EER_2[6,7] (E = Si, Ge, Sn, or Pb; R = large substituent) are protected by two large groups at each end of the double bond whereas the main group V elements involve only one substituent as in $R\ddot{E}{=}\ddot{E}R$ (E = P, As, Sb, or Bi).[4,5] The degree of crowding at the latter may be supplemented by the coordination of organometallic fragments to the lone pairs in which case the steric requirements for the R substituent at phosphorus become less stringent.[8-11] The synthesis of such compounds can readily be achieved by the direct reaction of Cl_2PR (R = large alkyl, aryl, amide, or aryloxide group) and $Na_2M(CO)_n$ (M = Fe or Cr, n = 4 or 5) as first demonstrated in this laboratory in 1983.[8]

In prior publications we have focussed on the reaction of $Na_2Fe(CO)_4$ and Cl_2PR and the variety of products obtained therefrom.[8,9,12] We now describe in greater detail the products obtained from the corresponding reaction of $Na_2Cr(CO)_5$ and Cl_2PR as illustrated in Scheme I. We also show that the compounds obtained are in many cases distinct and very different from the species derived from the reactions of $Na_2Fe(CO)_4$. Preliminary reports on three of the complexes described in this paper have appeared.[9,13] Further details are provided here. Related work[14] in another laboratory has involved reaction of $RPCl_2$ with the dinuclear organometallic substrate $Na_2M_2(CO)_{10}$ (R = Mes or $CH(SiMe_3)_2$, M = Cr, Mo, or W). Despite some similarity between the mono- and dinuclear reactants (two of the products from that paper were [*cis*-$(PMes)_2\{Cr(CO)_5\}_2$] (**1b**) and the phosphinidene [$\{Cr(CO)_5\}_2PMes$] (**4**)) the number of different products is actually quite remarkable.

Experimental Section

General Procedures. All experiments were performed using either modified Schlenk techniques under N_2 or a Vacuum Atmospheres HE 43-2 drybox under Argon. Solvents were freshly distilled under N_2 from Na/K alloy–benzophenone–ketyl and degassed twice immediately before use.

Physical Measurements. ^{31}P NMR spectra were obtained in C_6D_6 by using a Nicolet NT-200 spectrometer operating at 81 MHz. All ^{31}P spectra were referenced to external 85% H_3PO_4 and recorded with 2-W proton-decoupling unless otherwise noted. IR spectra (carbonyl region) were recorded on a Perkin-Elmer 180 or on an IBM IR/32 or IR/98 FT-IR spectrometers. All compounds gave satisfactory C and H analyses.

Starting Materials. The reagents $Na_2Cr(CO)_5$,[15] $MesPCl_2$,[16] $Me_3SiCH_2PCl_2$,[17] $(Me_3Si)_2CHPCl_2$,[18] $(Me_3Si)_2NPCl_2$,[18] and 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$[19] were prepared according to literature methods. Other reagents were obtained commercially and used as received.

Synthesis of Compounds 1–12. [*trans*-$(PMes)_2\{Cr(CO)_5\}_2$] (1a), [*cis*-$(PMes)_2\{Cr(CO)_5\}_2$] (1b), [$\{Cr(CO)_5\}_2(PHMes)_2$] (2), [$Cr(CO)_5\{$*cyclo*-$(PMes)_3\}$] (3), and [$\{Cr(CO)_5\}_2PMes$] (4). $Na_2Cr(CO)_5$ (0.952 g, 4 mmol) was dissolved in Et_2O (100 mL) and $MesPCl_2$ (0.884 g, 4 mmol) in Et_2O (50 mL) was added dropwise at 0 °C. The resulting dark red solution was stirred 12 h at room temperature. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel eluted with n-hexane to give 30% yield of dark red **1a** (mp 194–196 °C; ^{31}P NMR δ 419.9, IR (Nujol); 1949, 1967, 2003, 2054, 2077 cm^{-1}; 23% yield of orange red **1b**; mp 189–191 °C; ^{31}P NMR δ 396.7; IR (Nujol) 1936, 1946, 1959, 1992, 2061 cm^{-1}), purple **3** (15% yield; mp 259 °C; ^{31}P NMR δ − 43.7 (dd), −90.4 (dd), −113.3 (dd), J_{PP} = 224, 274, 147 Hz; IR (Nujol) 1939, 1965, 1967, 2004, 2056, 2077 cm^{-1}), and blue **4** (18% yield; mp 125–127 °C; ^{31}P NMR δ 1216; IR (Nujol) 1956, 1989, 2037, 2046, 2088 cm^{-1}). The same reaction in THF under similar conditions gave a red solution. The chromatographic separation (silica gel/n-hexane) resulted in **1a** (21% yield), **1b** (38% yield), **2** (13% yield), and **4** (5% yield).

[*trans*-$\{Cr(CO)_5\}_2\{$*cyclo*-$(PCH_2SiMe_3)_4\}$] (5) and [*trans*-$\{PCH_2SiMe_3\}_2\{Cr(CO)_5\}_2$] (6). $Na_2Cr(CO)_5$ (0.48 g, 2 mmol) was dissolved in THF (50 mL), and $Me_3SiCH_2PCl_2$ (0.38 g, 2 mmol) in hexane (20 mL) was added dropwise at room temperature. The resulting orange solution was stirred for 15 h, solvents were removed under reduced pressure, and the products were separated by column chromatography (silica gel/n-hexane). Slow cooling afforded pale yellow crystals of **5** (yield 30%; mp 192–194 °C, ^{31}P NMR δ 46.9 (t), −11.4 (t), J_{PP} = 165 Hz; IR (Nujol) 1922, 1937, 1949, 1985, 2055 cm^{-1}) and orange-yellow crystals of **6** (yield 12%; ^{31}P NMR δ 189; IR (Nujol) 1946, 1986, 2060, 2070 cm^{-1}).

[*trans*-$\{PCH(SiMe_3)_2\}_2Cr(CO)_5$] (7). Solid $Na_2Cr(CO)_5$ (0.24 g, 1 mmol) was added to $(Me_3Si)_2CHPCl_2$ (0.26 g, 1 mmol) in Et_2O (25 mL) at 0 °C. The resulting solution was stirred overnight. The volatiles were removed under vacuum; the residue was dissolved in n-hexane, filtered, and cooled to −20 °C. The crystals obtained were unsuitable for X-ray diffraction studies. A suitable crystal of this material was obtained from Et_2O solution: orange-yellow crystals; yield 45%; mp 109–114 °C; ^{31}P NMR δ 477.3 (d), 446.2 (d), J_{PP} = 510 Hz; IR (Nujol) 1934, 1955, 2060 cm^{-1}.

[*trans*-$\{PN(SiMe_3)_2\}_2Cr(CO)_5$] (8), [$\{Cr(CO)_5\}_2PN(SiMe_3)_2$] (9), and [*trans*-$Cr(CO)_4\{PN(SiMe_3)_2Cr(CO)_5\}_2$] (10). $Na_2Cr(CO)_5$ (1.19 g, 5 mmol) was dissolved in THF (100 mL) and $(Me_3Si)_2NPCl_2$ (1.31 g, 5 mmol) in THF (50 mL) was added dropwise at 0 °C. The resulting purple solution was stirred overnight at room temperature. The products

---

[1] Present address: Shell Development, Westhollow Research Center, Houston, TX 77001.

[2] A.P. Sloan Foundation Fellow 1985–1987.

[3] Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

[4] Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820.

[5] Cowley, A. H. *Polyhedron* **1984**, *3*, 389. Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 384. Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1.

[6] Goldberg, D.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261. West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[7] Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480. Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

[8] Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085.

[9] Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7750.

[10] Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7751.

[11] Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 977.

[12] Flynn, K. M.; Bartlett, R. A., Olmstead, M. M.; Power, P. P. *Organometallics* **1986**, *5*, 813.

[13] Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460.

[14] Lang, H.; Orama, O.; Huttner, G. *J. Organomet. Chem.* **1985**, *291*, 293.

[15] Ellis, J. E.; Hentges, S. G. Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79.

[16] The reported synthesis for $MesPCl_2$ by: Oshikawa, T.; Yamashita, M. *Chem. Ind. (London)* **1985**, 126, used with slight modifications. MesLi was prepared from n-BuLi and MesBr in Et_2O/hexane. The solid MesLi was separated by filtration and suspended in Et_2O, and 15% excess of PCl_3 was added at −20 °C. The mixture was worked up as described to give 70% yield of $MesPCl_2$.

[17] Seyferth, D.; Freyer, W. *J. Org. Chem.* **1961**, *26*, 2604.

[18] Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

[19] Flynn, K. M. Ph.D. Thesis, University of California Davis, 1985.

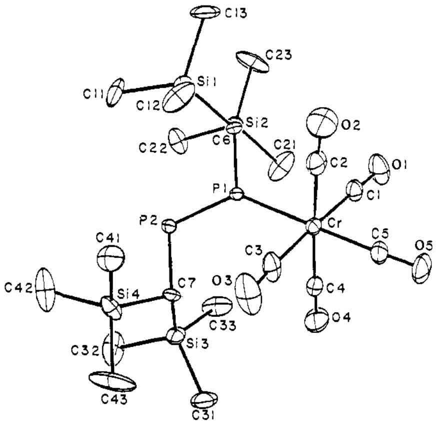


Figure 1. Computer-generated thermal ellipsoid (30% probability level) plot of **7**. Important bond distances (Å) and angles (deg): P(1)P(2) = 2.027 (3), P(1)C(6) = 1.824 (6), P(2)C(7) = 1.836 (6), CrP(1) = 2.360 (2), CrC(5) = 1.862 (8), O(5)C(5) = 1.155 (10), $CrC(cis)_{av}$ = 1.835, $C(cis)O(cis)_{av}$ = 1.140, $SiC(Me)_{av}$ = 1.847, $C(6)Si_{av}$ = 1.909, $C(7)Si_{av}$ = 1.894, CrP(1)C(6) = 120.1 (2), P(2)P(1)C(6) = 105.6 (2), P(1)P(2)C(7) = 105.9 (2), CrP(1)P(2) = 134.2 (1), Si(1)C(6)Si(2) = 117.6 (3), Si(3)C(7)Si(4) = 117.8 (4).

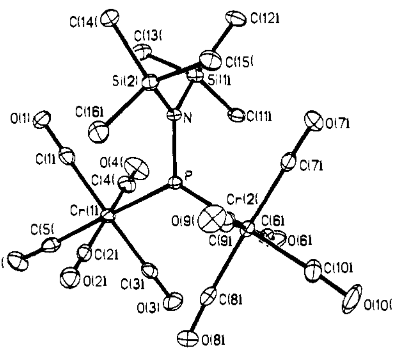


Figure 2. Computer-generated thermal ellipsoid (30% probability level) plot of **9**. Important bond distances (Å) and angles (deg) PCr(1) = 2.286 (1), PCr(2) = 2.290 (1), PN = 1.697 (3), NSi(1) = 1.783 (4), NSi(2) = 1.775 (3), CSi_{av} = 1.861, CrC_{av} = 1.907, Cr(1)PCr(2) = 128.2 (1), Cr(1)PN = 116.0 (1), Cr(2)PN = 115.8 (1), Si(1)NSi(2) = 120.6 (2), PNSi(2) = 120.3 (2), PNSi(1) = 119.1 (2). Angle between P and N planes = 76°.

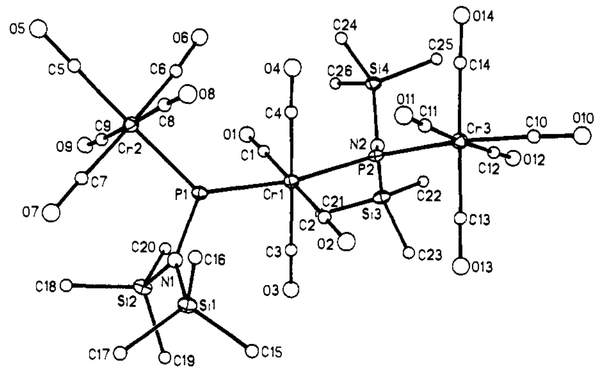


Figure 3. Computer-generated thermal ellipsoid plot of **10** (thermal ellipsoids at 40% probability, isotropic atoms given arbitrary fixed radius open circles). Important bond distances and angles (deg): Cr(1)P(1) = 2.277(2), Cr(1)P(2) = 2.288 (2), Cr(2)P(1) = 2.319 (2), Cr(3)P(2) = 2.321 (2), P(1)N(1) = 1.708 (5), P(2)N(2) = 1.691 (5), $Cr(1)C_{av}$ = 1.906, $Cr(2,3)C_{av}$ = 1.891, $CO\{Cr(1)\}_{av}$ = 1.148, $CO\{Cr2,3\}_{av}$ = 1.152, NSi_{av} = 1.779, N(1)P(1)Cr(1) = 116.3 (2), N(1)P(1)Cr(2) = 115.5 (2), Cr(1)P(1)Cr(2) = 128.2 (1), N(2)P(2)Cr(3) = 116.0 (2), N(2)P(2)Cr(1) = 114.5 (2), Cr(1)P(2)Cr(3) = 129.5 (1), Si(1)N(1)Si(2) = 120.1 (3), P(1)N(1)Si(2) = 121.4 (3), P(1)N(1)Si(1) = 118.4 (3), Si(3)N(2)Si(4) = 121.4 (3), P(2)N(2)Si(4) = 119.4 (3), P(2)N(2)Si(3) = 119.2 (3), P(1)Cr(1)P(2) = 169.6 (1). Angle between P(1) and P(2) planes = 96°.

were separated by column chromatography (silica gel/*n*-hexane) and crystallized from *n*-hexane to obtain orange crystals of **8** (18% yield; mp 95–97 °C; ^{31}P NMR δ 540.4 (d) 560.2 (d), J_{PP} = 631 Hz; IR (Nujol) 1955, 1986, 2063 cm^{-1}), purple crystals of **9** (45% yield; mp 182–184 °C; ^{31}P NMR δ 1277.7; IR (Nujol) 1951, 1962, 1981, 2002, 2036, 2064, 2074, 2085 cm^{-1}), and blue crystals of **10** (10% yield; mp 195 °C; ^{31}P NMR δ 1222.3; IR (Nujol) 1954, 1981, 2008, 2037, 2050, 2064, 2074 cm^{-1}).

$[Cr(CO)_5(PCl_2OC_6H_2$-2,6-*t*-Bu_2-4-Me)] (11) and $[\{Cr(CO)_5\}_2(POC_6H_2$-2,6-*t*-Bu_2-4-Me)] (12). Solid $Na_2Cr(CO)_5$ (0.71 g, 3 mmol) was added to 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$ (0.96 g, 3 mmol) in THF (100 mL) at 0 °C. The solution was stirred overnight at room temperature. Volatiles were removed under reduced pressure, and the residue was extracted into hexane. Fractional crystallization yielded **11** (mp 112–113 °C; ^{31}P NMR δ 190.4; IR (Nujol) 1943, 1944, 2084 cm^{-1}) and **12** (IR (Nujol) 1955, 1987, 2046 cm^{-1}). A third compound was also crystallized, but crystals suitable for X-ray diffraction have not yet been obtained.

X-ray Data Collection, Solutions, and Refinement of the Structures. A few conspicuous features of the structures of **7**, **9**, and **10** have been briefly described in preliminary communications.[9,13] Some further details are provided in Figures 1–3. The fast X-ray data collection technique[20a] was employed for all the structures described here. A Syntex $P2_1$ diffractometer equipped with a graphite monochromator and a modified LT-1 apparatus for low-temperature work was used. Crystallographic programs used were those of SHELXTL, version 4, installed on a Data General Eclipse computer. Scattering factors were from Vol. IV of ref 21. An absorption correction was applied by using the method described in ref 20b. All compounds were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. Suitable crystals were then attached to a glass fiber by using silicone grease and immediately placed in the low-temperature nitrogen stream. Table I (supplementary material) summarizes the crystal data and refinement for each compound. Notes on the solution of each structure and a description (with an illustrative figure) of the disorder in **1a** are also provided therein.

Results and Discussion

A summary of the product type with the corresponding ligands is given in Scheme I. In addition, important structural parameters as well as ^{31}P NMR and IR data are given in the Experimental Section. From these it can be readily seen that the size of the substituent on phosphorus plays a major role in determining the type of product obtained. It is apparent that each reaction can afford up to three or four products. For the smaller and also the more electronegative substituents the products are present in roughly equal amounts. With a large, less electronegative substituent such as $(Me_3Si)_2CH^-$ a preponderance of one product is obtained, e.g., the diphosphene complex **7**. Solvent effects are also evident. For example, in the reactions involving $MesPCl_2$ different proportions, and in some cases types, of product were obtained depending on whether the reaction was carried out in THF or Et_2O.

Reaction of $Na_2Cr(CO)_5$ with $(Me_3Si)_2CHPCl_2$ or $(Me_3Si)_2NPCl_2$. Initial work concerned the diphosphene complexes [*trans*-$\{PCH(SiMe_3)_2\}_2Cr(CO)_5$][9] (**7**) and [*trans*-$\{PN(SiMe_3)_2\}_2Cr(CO)_5$] (**8**).[13] Both exhibited an AB pattern at low field in their ^{31}P NMR spectra. The low shift values suggested a P–P double bond, and the AB pattern indicates two inequivalent phosphorus nuclei which suggested the structures indicated in Scheme I as a possibility. This was confirmed in the case of **7** by X-ray diffraction which showed that the diphosphene ligand $(Me_3Si)_2HCP{=}PCH(SiMe_3)_2$ is bound to a single $Cr(CO)_5$ fragment through one phosphorus atom only.[9] This structure is illustrated in Figure 1. This is in sharp contrast to the products obtained with smaller substituents[22] on phosphorus such as

---

(20) (a) Hope, H.; Nichols, B. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 158. (b) Program XABS. Hope, H.; Moezzi, B., unpublished work, University of California Davis, 1986. The program obtains an absorption tensor from $F_o - F_c$ differences.

(21) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1976; Vol. IV.

(22) We are grateful to a reviewer for providing a more quantitative basis for this statement by calculating the volumes of $-CH(SiMe_3)_2$ (146 Å^3), $-CH_2SiMe_3$ (83 Å^3), and Mes (102 Å^3) using QCPE program 509.

(23) This bonding pattern was observed simultaneously by Cowley and co-workers in the related $Fe(CO)_4$ system.[10] Further examples have appeared in ref 14.

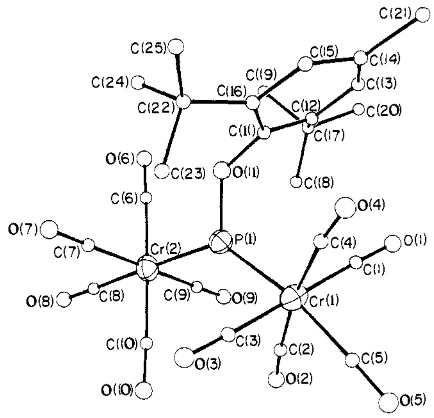


Figure 4. Computer-generated thermal ellipsoid plot of **12** (thermal ellipsoids at 30% probability, isotropic atoms given arbitrary fixed radius circles). Important bond distances (Å) and angles (deg) for each of the crystallographically independent molecules: P(1)Cr(1) = 2.276 (2), P(1)Cr(2) = 2.275 (2), P(1)O(11) = 1.643 (4), O(11)C(11) = 1.406 (8), $Cr(1)C_{av}$ = 1.898, $Cr(2)C_{av}$ = 1.909, $OC\{Cr(1)\}_{av}$ = 1.136, $OC\{Cr(2)\}_{av}$ = 1.131, Cr(1)P(1)Cr(2) = 132.3 (1), Cr(1)P(1)O(11) = 121.3 (2), Cr(2)P(1)O(11) = 106.3 (2), P(1)O(11)C(11) = 125.5 (3), P(2)Cr(3) = 2.278(2), P(2)Cr(4) = 2.274 (2), P(2)O(36) = 1.644 (4), O(36)C(36) = 1.411 (7), $Cr(3)C_{av}$ = 1.904, $Cr(4)C_{av}$ = 1.907, $OC\{Cr(3)\}_{av}$ = 1.133, $OC\{Cr(4)\}_{av}$ = 1.136, Cr(3)P(2)Cr(4) = 133.2 (1), Cr(3)P(2)O(36) = 121.0 (2), Cr(4)P(2)O(36) = 105.7 (2), P(2)O(36)C(36) = 127.2 (3).

$-CH_2SiMe_3$ or Mes which give either diphosphenes binding two $Cr(CO)_5$ fragments as in **1a** and **6** (see later in Figures 6 and 7) or the more highly aggregated species such as **3** or **5** (see later in Figures 8 and 9). The latter compound is in effect a dimer of **7** (ignoring the substituent on P). The size of the organometallic fragment also plays a role in determining the structure. For example two of the smaller $Fe(CO)_4$ moieties can be coordinated to the diphosphene $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$ whereas only one $Cr(CO)_5$ is readily coordinated. The steric effects of binding $Cr(CO)_5$ to the diphosphene in **7** is reflected in the orientation of the alkyl substituents. On C(6) both $SiMe_3$ groups are oriented away from the $Cr(CO)_5$ over the PP double bond whereas on C(7) they are oriented to the same side as the phosphorus lone pair away from the PP double bond. The ^{31}P NMR of the corresponding amido-substituted compound **8** is shifted approximately 88 ppm downfield in comparison to the alkyl analogue **7**. This is expected on the basis of the greater electronegativity of the substituent.

Although a very small amount of a purple material, presumably the phosphinidene complex $[\{(OC)_5Cr\}_2PCH(SiMe_3)_2]$, is produced from the reaction of $(Me_3Si)_2CHPCl_2$ and $Na_2Cr(CO)_5$, the same is not true for the reaction with the isoelectronic $(Me_3Si)_2NPCl_2$. Here major amounts of the phosphinidenes $[\{Cr(CO)_5\}_2PN(SiMe_3)_2]^{13}$ (**9**) and $[$*trans*-$Cr(CO)_4\{PN(SiMe_3)_2Cr(CO)_5\}_2]^{13}$ (**10**) are readily separated through column chromatography on silica gel. This result is somewhat unexpected in view of the similar sizes of $CH(SiMe_3)_2$ and $N(SiMe_3)_2$. Even if it was assumed that $CH(SiMe_3)_2$ occupied more space (C–Si longer than N–Si) than $N(SiMe_3)_2$, a steric reason for the differences in product distribution could hardly be sustained in view of the results when the substituent is the smaller CH_2SiMe_3 or Mes group. In the case of these ligands no significant amounts of products similar to **9** and **10** were seen. A clue to the large percentage of phosphinidene produced may come from the observation that such products are also found in the reaction with 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$. The latter is also fairly sterically demanding in addition to having an electronegative atom attached to phosphorus. It has been shown[24] that a significant feature of the bonding in phosphinidene complexes is a back-bonding involving electron transfer from transition metal d orbitals to an empty p orbital on phosphorus. Such a process would be enhanced by electronegative substituents on phosphorus. Also, the electronegative groups tend to weaken PP double bonds as demonstrated by slightly longer PP distances. Thus, electronic as well as steric effects appear to be intimately involved in determining which products will be obtained.

The structures of both phosphinidenes **9** and **10** have been determined by X-ray diffraction.[13] These are illustrated in Figures 2 and 3. The structure of **9** was in fact the first structural characterization of a chromium phosphinidene complex of this type although many phosphinidene and arsinidene derivatives of other transition metals had been previously reported.[24] The phosphorus atom is in the expected trigonal-planar configuration. The angles and distances surrounding phosphorus are close to those seen in other reported phosphinidenes.[14] The P–N distance, however, is somewhat short at 1.697 (3) Å. This is shorter than the distances seen in normal $\rangle P{-}N\langle$ bonds which involve lone pair repulsions whereas in the metal phosphinidenes this interaction is nonexistent. The ^{31}P chemical shift, 1278 ppm, and the purple color are in line with the bonding theories for other metal phosphinidenes.

The bis(phosphinidene) complex **10** with two phosphinidene ligands bonded to one metal remains the only example of this class of compound to have been reported.[13] This intensely blue-colored compound is the third and smallest fraction of the three compounds arising from the reaction of $Cl_2PN(SiMe_3)_2$ and $Na_2Cr(CO)_5$. Its synthesis is, however, quite reproducible and sufficient quantities of the thermally robust material (mp 195 °C) can readily be isolated for adequate spectroscopic characterization. The ^{31}P NMR spectrum reveals a singlet at 1222 ppm which is close to the value for compound **9**. The structure of **10** involves a central chromium substituted by four carbonyl and two bridging phosphinidene ligands in the trans positions as illustrated in Figure 3. The P–N distances are again somewhat short presumably for the same reasons as in **9**. The P–Cr distances to the central and terminal chromium atoms are slightly (ca. 0.04 Å) different. The values for the shorter (central) Cr–P distances are almost identical with the values in **8**. The long terminal Cr–P distances (ca. 2.32 Å) imply a weaker interaction between these two atoms. This allows stronger back-bonding to the CO in $Cr(CO)_5$ trans to the phosphinidene, and this is reflected in a somewhat longer than average trans CO bond. A conspicuous feature of the structure **10** is that the two CrPNCr planes are roughly mutually perpendicular so that the core geometry resembles that of allene.

Reaction of $Na_2Cr(CO)_5$ with 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$. A chromium phosphinidene complex, **12**, is also among the products from the reaction involving 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$. This structure is illustrated in Figure 4. Its structure is significantly different in the sense that the angles surrounding phosphorus show considerable asymmetry. Angular asymmetry has been previously noted in the phosphinidene $[\{\eta^5\text{-}(C_5H_5)(CO)Co\}_2PAr]$,[25] and the angles were thought to resemble those for σ-diphosphene and σ-phosphaalkene complexes. The large distortion in the angles of **12** are rather more probably due to steric effects induced by the large group and the low POC angle. There is bending in the CrCO moieties nearest the bulky aryloxo group where angles of as low as 173.1 (6)° are seen. The corresponding distortions in the carbonyls on Cr(2) are very slight, ~1°. The CrP distances are marginally shorter than those seen in the amido-substituted phosphinidene **9** perhaps due to the increased electrophilic character of the phosphorus atom. Some of the phosphane complex **11** (illustrated in Figure 5) as well as other unidentified products are also obtained in this reaction.

Reaction of $Na_2Cr(CO)_5$ with $Me_3SiCH_2PCl_2$ and $MesPCl_2$. The symmetrically substituted (*trans*-diphosphene)bis(chromium pentacarbonyl) complexes **1a** and **6** may be isolated from the reaction mixture involving $MesPCl_2$ and $Me_3SiCH_2PCl_2$ in Et_2O. The lowered steric requirements of the smaller Mes and CH_2SiMe_3 groups permit coordination of two $Cr(CO)_5$ fragments. Important structural parameters for these diphosphenes are given in Figures 6 and 7. Complex **1a** has been reported but not structurally characterized by Huttner and co-workers.[14] The most interesting

---

(24) Huttner, G. *Pure Appl. Chem.* **1986**, *24*, 585. Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406.

(25) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakuski, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1267.

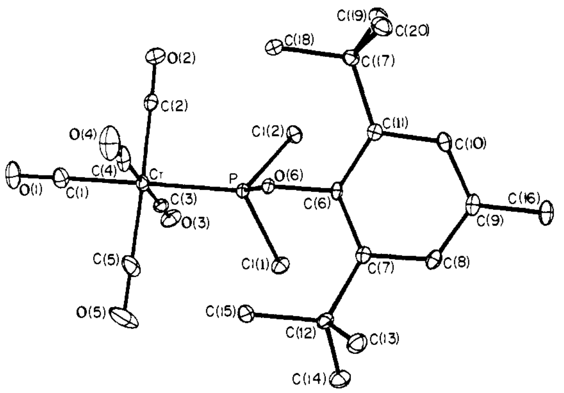


Figure 5. Computer-generated thermal ellipsoid (30% probability level) plot of **11**. Important bond distances (Å) and angles (deg): CrP = 2.259 (1), P–Cl (1) = 2.056 (1), P–Cl (2) = 2.051 (1), P–O (6) = 1.599 (1), O(6)C(6) = 1.425 (2), CrC_{av} = 1.905, CO_{av} = 1.138, Cl(1)PCl(2) = 96.0 (1), Cl(1)PO(6) = 104.3 (1), Cl(2)PO(6) = 104.7 (1), PO(6)C(6) = 124.7 (1).

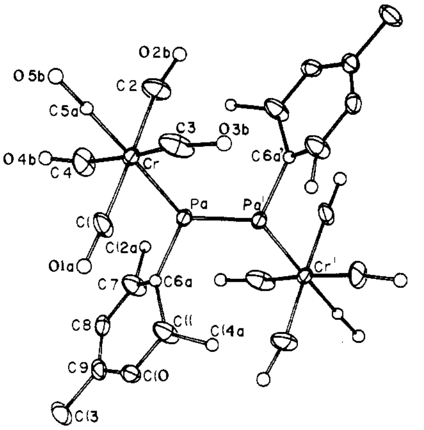


Figure 6. Computer-generated thermal ellipsoid plot of **1a** (disorder not shown, thermal ellipsoids at 30% probability level, isotropic atoms given arbitrary fixed radius circles). Important bond distances (Å) and angles (deg): CrPa = 2.329 (4), PaPa′ = 2.037 (7), PaC(6a) = 1.825 (11), CrC_{av} = 1.867, CrPaPa′ = 136.4 (2), C(6a)PaPa′ = 104.6 (5), CrPaC(6a) = 119.0 (5).

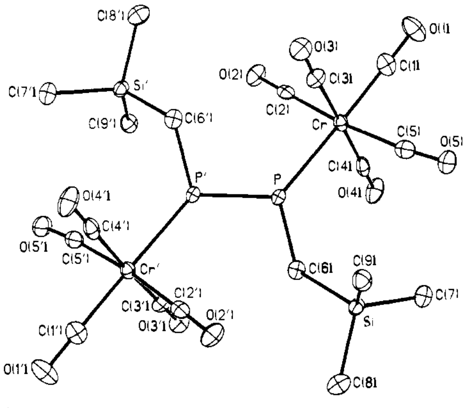


Figure 7. Computer-generated thermal ellipsoid (50% probability level) plot of **6**. Important bond distances (Å) and angles (deg): PP′ = 2.035(9), Cr–P = 2.352 (10), PC(6) = 1.829 (9), CrC(1) = 1.872 (10), $CrC(2\text{-}5)_{av}$ = 1.912, C(1)O(1) = 1.145 (10), CO(2-5) = 1.138, C(6)Si = 1.902 (9), $SiC(7\text{-}9)_{av}$= 1.852, CrPP′ = 129.1 (3), CrPC(6) = 123.1 (3), C(6)PP′ = 106.8 (3).

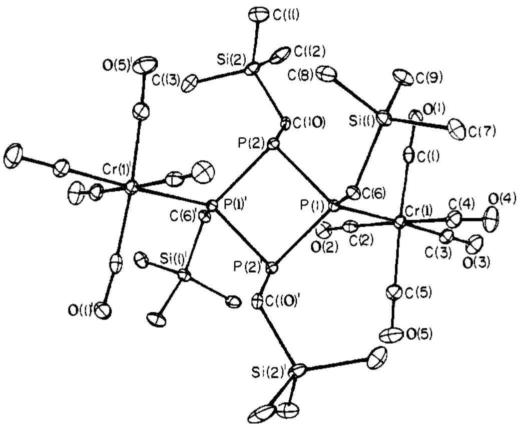


Figure 8. Computer-generated thermal ellipsoid (30% probability level) plot of **5**. Important bond distances (Å) and angles (deg): P(1)P(2) = 2.241 (2), P(1)P(2)′ = 2.247 (2), P(1)Cr(1) = 2.399 (2), P(1)C(6) = 1.833 (6), P(2)C(10) = 1.848 (5), Si(1)C(6) = 1.898 (5), C(10)Si(2) = 1.878 (6), $SiC(Me)_{av}$ = 1.860, P(1)P(2)P(1)′ = 89.7 (1), P(2)P(1)P(2)′ = 90.3 (1), Cr(1)P(1)P(2) = 124.4 (1), Cr(1)P(1)P(2)′ = 111.7 (1), Cr(1)P(1)C(6) = 118.1 (2), P(1)P(2)C(10) = 106.6 (2), P(1)′P(2)C(10) = 108.6 (2).

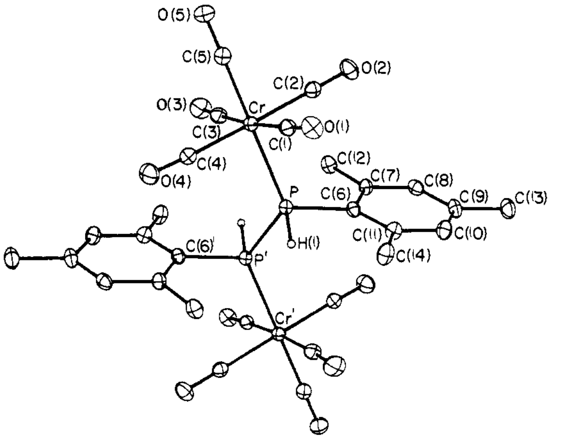


Figure 9. Computer-generated thermal ellipsoid (30% probability level) plot of **2**. Important bond distances (Å) and angles (deg): PP′ = 2.253 (2), CrP = 2.384 (1), PC(6) = 1.841 (4), PH(1) = 1.308 (39), CrPC(6) = 118.0 (1), H(1)PC(6) = 94.7 (15), HPP′ = 95.5 (20), H(1)PCr = 115.8 (15).

features are the P–P distances which are 2.037 (7) and 2.032 (6) Å for **1a** and 2.035 (9) Å seen in **6**. A longer value 2.067 (3) Å has been observed for the double bond in the *trans*-diphosphene complex $[\{Cr(CO)_5\}_2(POC_6H_2\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}Me)_2]$ which was obtained from the reaction of $Na_2Cr_2(CO)_{10}$ with 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$. The longer P–P distances in the latter are presumably due to the more electronegative substituent. A similar lengthening has been seen in the isoelectronic iron diphosphene complexes $[trans\text{-}\{PR\}_2(Fe(CO)_4)_2]$ (R = $CH(SiMe_3)_2$,[8] 2.039 (1) Å; R = $N(SiMe_3)_2$, 2.053 (1) Å).[13] The longer (weaker) P–P bonds observed with more electronegative substituents along with the lower proportions of diphosphenes in the products are also consistent with the observation that more electronegative substituents tend to favor more phosphinidene and bridged products.

The other major product arising from the reaction of $Me_3SiCH_2PCl_2$ is a four-membered cyclotetraphosphane bound symmetrically to two $Cr(CO)_5$ fragments. Its structure is illustrated in Figure 8. Such species have not hitherto been reported as a product from the title reaction. From the stoichiometric point of view **5** could be considered a dimer of **7** with $CH(SiMe_3)_2$ replaced by CH_2SiMe_3. Dimerization may be a consequence of the reduced steric requirements of the smaller alkyl group. One feature of interest is the planarity of the almost square P_4 ring which contrasts with the usual butterfly configuration. The P–P distances are within the normal range for P–P single bonds but nearer the higher end of the envelope. The Cr–P distance 2.399 (2) Å is somewhat longer than the values found in **7** perhaps due to the higher phosphorus coordination number. The ^{31}P NMR involves an expected AB_2 pattern with the coordinated phosphorus atom appearing well downfield of the free phosphorus ring member.

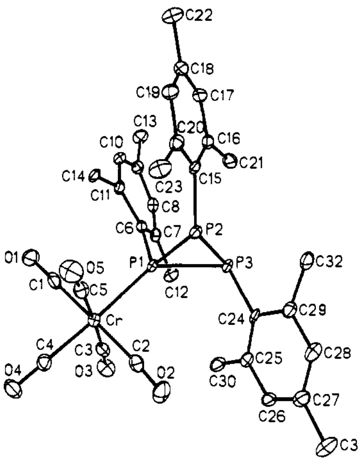


Figure 10. Computer-generated thermal ellipsoid (30% probability level) plot of **3**. Important bond distances (Å) and angles (deg): P(1)P(2) = 2.209 (1), P(2)P(3) = 2.208 (1), P(1)P(3) = 2.246 (1), CrP(1) = 2.396 (1), P(1)C(6) = 1.830 (4), P(2)C(15) = 1.845 (5), P(3)C(24) = 1.842 (4), P(2)P(1)P(3) = 59.4 (1), P(1)P(2)P(3) = 61.1 (1), P(1)P(3)P(2) = 59.4 (1), C(6)P(1)P(2) = 109.6 (1), C(6)P(1)P(3) = 98.9 (1), CrP(1)P(2) = 118.9 (1), CrP(1)P(3) = 135.6 (1), P(1)P(2)C(15) = 113.9 (1), P(3)P(2)C(15) = 114.3 (1), P(1)P(3)C(24) = 111.2 (1), P(2)P(3)C(24) = 98.2 (1).

The reaction involving $MesPCl_2$ in Et_2O afforded not only the diphosphene complexes **1a** and **1b** but also the previously unreported cyclotriphosphane complex **3** in addition to a blue colored band identified by ^{31}P NMR (δ 1218), IR, and melting point data as the species $[\{(OC)_5Cr\}_2PMes]$ (**4**). When THF solvent was used, no **3** was detected. Instead **2** was obtained in addition to **1a**, **1b**, and **4**. The appearance of **2** is somewhat unexpected, and its presence in the reaction mixture as a significant product is reproducible. The structure of **2** is illustrated in Figure 9. The appearance of products involving P–H bonds has been noted in other similar systems[26] and is probably due to H abstraction from the solvent. The structure of **2** shows clearly that each phosphorus is pyramidal and that the P–P distance 2.253 (2) Å is consistent with a single bond.

The appearance of a cyclotriphosphane complex **3**, similar to the cyclotetraphosphane complex **5**, among the products of the reaction between $RPCl_2$ and carbonylmetalate salt has not been hitherto reported. However, uncomplexed cyclic species have been observed in the corresponding reduction of $(Me_3Si)_2CHPCl_2$ by magnesium.[26] The three-membered ring in **3** suggests that the mesityl group is more sterically demanding than CH_2SiMe_3. Among cyclopolyphosphanes the three-membered rings are less common[28,29] and require large groups to provide the kinetic stabilization necessary for their isolation under ambient conditions.[29] A free cyclotriphosphane has been structurally characterized in the solid state.[30] In addition, the structure of a complex very similar to **3**, the species ($[Cr(CO)_5\{$*cyclo*-$(t\text{-}BuP)_3\}]$, has been reported.[31] Another related complex is $[\{Mn(\eta^5\text{-}C_5H_5)(CO)_2\}_3\{$*cyclo*-$(PPh)_3\}]$ which has been known for a number of years.[32] Both of these complexes were synthesized by different routes from **3**. The structural details of **3** (Figure 10) involve normal P–P distances within the three-member ring. Some evidence of crowding is apparent in the slightly longer P(1)–P(3) and Cr–P(1) distances and the CrC(2)O(2), CrC(3)O(3), and CrC(5)O(5) angles. It is evident from the structure that the three phosphorus atoms are inequivalent, and this is confirmed by the ^{31}P NMR spectrum. P(1) appears at −43.76 ppm whereas P(2) and P(3) appear at −90.4 and −113.3 ppm. The coupling constants are J_{12} = 223.6, J_{13} = 273.5, and J_{23} = 146.8 Hz. These shifts and coupling constants are very similar to those noted previously by Baudler and coworkers.[29]

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Summary of data collection and refinement, tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates, and a figure illustrating the disorder in **1a** (38 pages). Ordering information is given on any current masthead page.

---

(26) Borm, J.; Knoll, K.; Zsolnai, L.; Huttner, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 532.

(27) Bertrand, G.; Couret, C.; Escudie, J.; Majid, S.; Majoral, J. P. *Tetrahedron Lett.* **1982**, 3567.

(28) Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 492.

(29) Baudler, M.; Ständeke, H.; Borgandt, M.; Strabel, H. *Naturwissenschaften* **1965**, *52*, 345. Cowley, A. H.; Furtsch, T. A.; Dierdorf, D. S. *J. Chem. Soc., Chem. Commun.* **1970**, 523. Baudler, M. Bock, M. *Z. Anorg. Allg. Chem.* **1973**, *395*, 37.

(30) Hahn, J.; Baudler, M.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 797. Tebbe, K.-F.; Feher, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 37.

(31) Baudler, M.; Salzer, F.; Hahn, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1529.

(32) Huttner, G.; Müller, H. D.; Frank, A.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 572.