is *not* operative in the chloramination of ammonia in alkali hydroxide solutions. The factors which determine which mechanism operates in the various instances are not evident at this time.

The results reported here indicate no unexpected products except the formation of *sym*-hexahydro-1,4-dimethyltetrazine and water when the reaction was carried out in the presence of sodium methoxide. These products and the drop in the concentration of total N–N bonded material on storing the reaction solutions over a period of time are attributed to the aerial oxidation[24] of methylhydrazine or other N–N bonded compounds during filtration, distillation, and handling, although care was taken to minimize contact of these products with the atmosphere.

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Registry No. CH_3NH_2, 74-89-5; NH_2Cl, 10599-90-3; $[(CH_3)_2C{=}NNH_2CH_3]Cl$, 73531-89-2; CH_3NHNH_2, 60-34-4; NH_2NH_2, 302-01-2; $CH_3NHN{=}CH_2$, 36214-48-9; $(CH_3NNHCH_2)_2$, 695-20-5.

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(25) Although glass wool filters are used in the chloramine generator to check the flow of NH_4Cl from the chloramine generator to the reaction vessel, this does not completely prevent NH_4Cl from going to the reaction vessel. This NH_4Cl then reacts with CH_3ONa to form NaCl, NH_3, and CH_3OH. The observed amount of NaCl, therefore, was more than the calculated amount.

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Synthesis and Molecular Geometry of *fac*-$Cr(CO)_3(PEt_3)_3$

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Structural studies on octahedral phosphine-substituted metal carbonyl complexes such as $Cr(CO)_5(PPh_3)$,[1] $W(CO)_5[P(t\text{-}Bu)_3]$,[2] {*cis*-$Mn(CO)_2[P(OMe)_2Ph]_4$}{$PF_6$},[3] fac-$Cr(CO)_3(PH_3)_3$,[4] and *cis*-$Cr(CO)_2(PH_3)_4$[5] have revealed only very minor geometric irregularities attributable to steric interaction between the phosphine ligands and the $M(CO)_x$ fragment. The role of ligand size in the *reactions* of these octahedral complexes is, nonetheless, clear-cut.[6–8] Thus, Reimann and Singleton[6] have shown that the smaller phosphine and phosphite ligands react with $M(CO)_5Br$ (M = Mn, Re) replacing *four* carbonyl ligands, whereas larger ligands replace no more than *two* ligands. Studies on the group 6 metal carbonyls also provide evidence for steric interactions both in reactions and in product distribution.[8,9] Thus, with $Cr(CO)_6$, the most highly substituted complex obtainable with PPh_3 is *trans*-$Cr(CO)_4(PPh_3)_2$, whereas smaller ligands (such as PH_3) yield species of stoichiometry $Cr(CO)_2L_4$.[5,9]

Table I. Experimental Data for the X-ray Diffraction Study of *fac*-$Cr(CO)_3(PEt_3)_3$

A. Crystal Parameters[a] at 26 °C

cryst system: monoclinic
space group: $P2_1$
$a = 8.4198\ (12)$ Å
$b = 16.2973\ (35)$ Å
$c = 10.1002\ (19)$ Å
$\beta = 105.094\ (17)°$
$V = 1338.1$ Å^3
$Z = 2$
mol wt 490.1
ρ(calcd) = 1.217 g/cm^3

B. Measurement of Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda} = 0.710\ 730$ Å)
monochromator: highly oriented graphite, equatorial
reflctns measd: $+h, +k, \pm l$
2θ range: 4.5–45.0°
scan type: θ(crystal)–2θ(counter)
scan range: $[2\theta(\text{Mo K}\alpha_1) - 1.0]° \rightarrow [2\theta(\text{Mo K}\alpha_2) + 1.0]°$
reflctns collected: 1972 total, 1830 independent
stds: 3 every 47 reflections, no significant decay
abs coeff: $\mu = 6.11$ cm^{-1}; no correction necessary
ignorance factor: $p = 0.015$

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ component of the 24 reflections of the forms $\{\bar{1}81\}$, $\{511\}$, $\{125\}$, $\{163\}$, $\{\bar{5}52\}$, and $\{\bar{5}25\}$, all with $2\theta = 20.0\text{–}29.0°$.

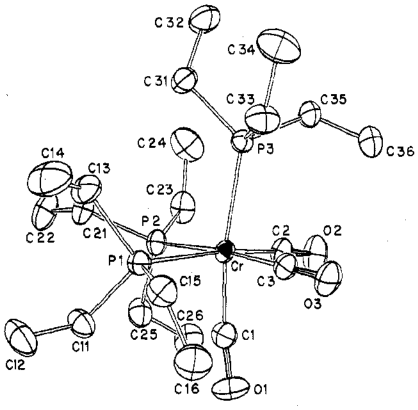

Figure 1. Labeling diagram for *fac*-$Cr(CO)_3(PEt_3)_3$ (ORTEP-II diagram; 50% ellipsoids; hydrogen atoms omitted).

The cis and trans isomers of $Mo(CO)_4L_2$ have been prepared, and steric interactions have been invoked to interpret the reactions of the cis complexes.[8] The most common method of measuring steric interactions involves the "cone angle" of the ligand, as determined from molecular models.[7] This has been correlated with reaction rates, although it should be noted that (in some cases) the crystallographically determined cone angle differs from that obtained from models.[10]

In order to obtain further information on steric interactions in "crowded" phosphine-substituted $M(CO)_6$ derivatives, we have undertaken a single-crystal X-ray diffraction study of *fac*-$Cr(CO)_3(PEt_3)_3$, which was prepared as described below. (Note that the direct reaction of $Cr(CO)_6$ with PEt_3 yields only cis and trans isomers of $Cr(CO)_4(PEt_3)_2$.[11])

Experimental Section

Preparation of *fac*-$Cr(CO)_3(PEt_3)_3$. A sample of 0.5 g of $CrCl_2$ was suspended in toluene (30 mL). PEt_3 (1.0 mL) was added to the suspension and stirred vigorously for 30 min, during which time the solution changed from green to very intense blue. $Na^+[Mn(CO)_5^-]$(0.8 g) was added and stirred for 1 h during which the solution became

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Table II. Final Positional Parameters (with Esd's) for *fac*-Cr(CO)$_3$(PEt$_3$)$_3$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cr	−0.11698 (8)	0.00000 (0)	−0.16627 (7)	H(23B)	−0.3976	−0.1920	−0.4464
P(1)	−0.14650 (15)	−0.01595 (9)	0.06438 (12)	H(25A)	−0.0723	−0.2180	−0.1330
P(2)	−0.2707 (2)	−0.12491 (10)	−0.24500 (13)	H(25B)	−0.2071	−0.2635	−0.2425
P(3)	−0.33772 (15)	0.09998 (9)	−0.23681 (13)	H(31A)	−0.5720	0.0192	−0.2617
C(1)	0.0747 (7)	−0.0579 (4)	−0.1115 (6)	H(31B)	−0.5776	0.0917	−0.1634
O(1)	0.2039 (5)	−0.0885 (3)	−0.0805 (5)	H(33A)	−0.3042	0.1733	−0.0340
C(2)	−0.0809 (6)	0.0022 (4)	−0.3365 (5)	H(33B)	−0.2015	0.2140	−0.1232
O(2)	−0.0515 (5)	0.0009 (3)	−0.4429 (4)	H(35A)	−0.3630	0.1030	−0.4703
C(3)	0.0182 (6)	0.0894 (4)	−0.1165 (5)	H(35B)	−0.4407	0.1816	−0.4271
O(3)	0.1102 (5)	0.1436 (3)	−0.0902 (4)	H(12A)	−0.0655	−0.1924	0.3044
C(11)	−0.0865 (7)	−0.1188 (4)	0.1383 (6)	H(14A)	−0.4839	0.0344	0.2253
C(12)	−0.1006 (10)	−0.1377 (5)	0.2810 (7)	H(16A)	0.2293	0.0740	0.2818
C(13)	−0.3536 (7)	0.0006 (5)	0.0971 (5)	H(22A)	−0.5986	−0.2520	−0.1622
C(14)	−0.3706 (9)	0.0300 (6)	0.2283 (8)	H(24A)	−0.5629	−0.0971	−0.5809
C(15)	−0.0148 (7)	0.0524 (4)	0.1924 (5)	H(26A)	0.0390	−0.2686	−0.3024
C(16)	0.1690 (8)	0.0369 (5)	0.2149 (7)	H(32A)	−0.7972	0.0988	−0.3510
C(21)	−0.4366 (7)	−0.1599 (4)	−0.1682 (6)	H(34A)	−0.3992	0.3042	−0.0926
C(22)	−0.5166 (9)	−0.2426 (5)	−0.2096 (8)	H(36A)	−0.2150	0.2161	−0.5032
C(23)	−0.3701 (8)	−0.1358 (5)	−0.4294 (6)	H(12B)	−0.2117	−0.1316	0.2840
C(24)	−0.5227 (10)	−0.0867 (5)	−0.4855 (7)	H(12C)	−0.0331	−0.1008	0.3443
C(25)	−0.1382 (8)	−0.2165 (4)	−0.2251 (7)	H(14B)	−0.3198	0.0822	0.2470
C(26)	−0.0244 (9)	−0.2198 (4)	−0.3194 (7)	H(14C)	−0.3189	−0.0074	0.2983
C(31)	−0.5588 (6)	0.0768 (4)	−0.2489 (6)	H(16B)	0.1982	0.0447	0.1311
C(32)	−0.6929 (7)	0.1169 (5)	−0.3590 (7)	H(16C)	0.1939	−0.0178	0.2458
C(33)	−0.3059 (7)	0.1918 (4)	−0.1236 (7)	H(22B)	−0.4356	−0.2844	−0.1869
C(34)	−0.4306 (10)	0.2617 (5)	−0.1586 (8)	H(22C)	−0.5656	−0.2430	−0.3056
C(35)	−0.3482 (7)	0.1460 (4)	−0.4047 (7)	H(24B)	−0.4983	−0.0299	−0.4713
C(36)	−0.1988 (8)	0.1948 (5)	−0.4132 (7)	H(24C)	−0.6038	−0.1018	−0.4400
H(11A)	−0.1532	−0.1575	0.0784	H(26B)	0.0468	−0.1735	−0.3026
H(11B)	0.0253	−0.1267	0.1387	H(26C)	−0.0879	−0.2191	−0.4121
H(13A)	−0.4095	0.0389	0.0304	H(32B)	−0.6800	0.1023	−0.4466
H(13B)	−0.4086	−0.0508	0.0818	H(32C)	−0.6856	0.1748	−0.3483
H(15A)	−0.0373	0.1074	0.1625	H(34B)	−0.5363	0.2418	−0.1578
H(15B)	−0.0416	0.0448	0.2773	H(34C)	−0.4336	0.2825	−0.2471
H(21A)	−0.3914	−0.1612	−0.0716	H(36B)	−0.1048	0.1601	−0.3925
H(21B)	−0.5214	−0.1198	−0.1903	H(36C)	−0.1825	0.2387	−0.3493
H(23A)	−0.2921	−0.1201	−0.4778				

[a] All hydrogen atoms were assigned isotropic thermal parameters of 7.0 Å^2.

Table III. Final Anisotropic Thermal Parameters for Nonhydrogen Atoms in *fac*-Cr(CO)$_3$(PEt$_3$)$_3$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	2.86 (3)	3.31 (4)	2.57 (3)	−0.10 (3)	1.10 (3)	−0.09 (3)
P(1)	3.67 (6)	3.99 (7)	2.55 (5)	0.33 (5)	1.05 (4)	0.05 (5)
P(2)	4.23 (6)	3.56 (6)	3.12 (6)	−0.54 (5)	1.58 (5)	−0.42 (5)
P(3)	3.09 (5)	3.57 (6)	3.11 (6)	0.03 (5)	0.88 (4)	0.19 (5)
C(1)	4.7 (3)	4.7 (3)	3.6 (3)	0.5 (2)	1.6 (2)	0.0 (2)
O(1)	4.1 (2)	7.7 (3)	8.3 (3)	2.5 (2)	1.3 (2)	−0.3 (2)
C(2)	4.0 (2)	4.1 (2)	3.4 (2)	−0.8 (2)	1.6 (2)	−0.8 (2)
O(2)	8.8 (3)	7.5 (2)	4.2 (2)	−2.2 (3)	4.0 (2)	−1.1 (2)
C(3)	3.9 (2)	4.3 (3)	3.3 (2)	0.0 (2)	1.7 (2)	−0.1 (2)
O(3)	5.0 (2)	5.7 (2)	6.3 (2)	−2.3 (2)	1.4 (2)	−0.6 (2)
C(11)	6.3 (3)	4.7 (3)	3.7 (3)	1.1 (3)	1.8 (2)	0.7 (2)
C(12)	11.4 (5)	6.8 (4)	5.3 (3)	3.4 (4)	3.9 (3)	2.3 (3)
C(13)	4.8 (2)	8.6 (4)	4.0 (2)	1.4 (3)	2.3 (2)	0.5 (4)
C(14)	7.7 (4)	12.0 (7)	8.0 (4)	3.1 (4)	3.4 (3)	−1.2 (4)
C(15)	5.3 (3)	5.8 (3)	3.4 (2)	−0.2 (3)	0.7 (2)	−0.4 (2)
C(16)	5.8 (3)	9.0 (5)	5.1 (3)	−1.0 (3)	−0.7 (3)	−0.2 (3)
C(21)	5.2 (3)	5.1 (3)	4.9 (3)	−1.7 (2)	2.6 (2)	−0.7 (2)
C(22)	6.9 (4)	7.2 (4)	9.2 (5)	−3.5 (4)	3.9 (4)	−1.5 (4)
C(23)	6.6 (4)	6.1 (4)	3.4 (3)	−1.6 (3)	1.3 (2)	−0.9 (3)
C(24)	9.4 (5)	7.0 (4)	5.2 (3)	−0.4 (4)	−0.0 (3)	−0.3 (3)
C(25)	7.0 (4)	3.8 (3)	6.1 (3)	0.3 (3)	3.2 (3)	0.0 (2)
C(26)	8.2 (4)	5.9 (4)	7.2 (4)	1.2 (3)	4.4 (4)	−0.8 (3)
C(31)	3.7 (3)	5.0 (3)	5.4 (3)	−0.1 (2)	1.5 (2)	0.0 (2)
C(32)	3.6 (3)	8.8 (5)	6.5 (3)	0.1 (3)	0.5 (2)	0.9 (3)
C(33)	5.5 (3)	4.4 (3)	6.2 (3)	0.5 (3)	0.9 (3)	−1.3 (3)
C(34)	9.3 (5)	5.1 (4)	7.4 (4)	1.9 (3)	0.9 (4)	−1.4 (3)
C(35)	4.2 (3)	6.3 (4)	4.5 (3)	0.2 (2)	1.5 (2)	2.1 (3)
C(36)	6.0 (3)	7.5 (4)	8.0 (4)	−0.1 (3)	2.4 (3)	3.9 (4)

[a] The anisotropic thermal parameters are in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

dark green. The solution was concentrated under reduced pressure and filtered through a Celite-covered fine frit. The resulting dark green solution was separated on a silica gel column with toluene as an eluant. The third band (light orange) contained *fac*-Cr(CO)$_3$-

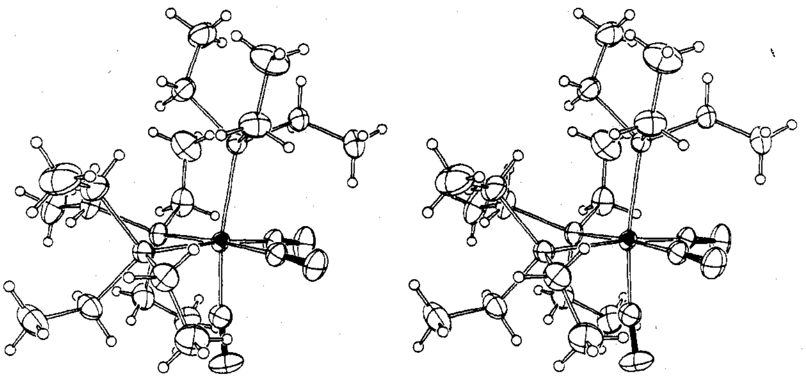

Figure 2. Stereoscopic view of *fac*-$Cr(CO)_3(PEt_3)_3$, with hydrogen atoms included in idealized (staggered) positions.

Table IV. Interatomic Distances (Å) and Esd's for *fac*-$Cr(CO)_3(PEt_3)_3$

(a) Chromium-Ligand Bond Lengths			
Cr-P(1)	2.420 (2)	Cr-C(1)	1.827 (6)
Cr-P(2)	2.432 (2)	Cr-C(2)	1.822 (5)
Cr-P(3)	2.435 (2)	Cr-C(3)	1.838 (6)
(b) Carbon-Oxygen Distances			
C(1)-O(1)	1.163 (8)	C(3)-O(3)	1.158 (7)
C(2)-O(2)	1.164 (6)		
(c) Phosphorus-Carbon Distances			
P(1)-C(11)	1.850 (6)	P(2)-C(25)	1.843 (7)
P(1)-C(13)	1.877 (6)	P(3)-C(31)	1.872 (6)
P(1)-C(15)	1.842 (6)	P(3)-C(33)	1.859 (6)
P(2)-C(21)	1.855 (6)	P(3)-C(35)	1.835 (7)
P(2)-C(23)	1.841 (6)		
(d) Carbon-Carbon Distances			
C(11)-C(12)	1.508 (9)	C(25)-C(26)	1.518 (10)
C(13)-C(14)	1.450 (10)	C(31)-C(32)	1.511 (9)
C(15)-C(16)	1.526 (10)	C(33)-C(34)	1.528 (10)
C(21)-C(22)	1.516 (10)	C(35)-C(36)	1.509 (10)
C(23)-C(24)	1.494 (11)		

Table V. Interatomic Angles (Deg) with Esd's for *fac*-$Cr(CO)_3(PEt_3)_3$

(a) Angles about Chromium			
P(1)-Cr-P(2)	92.61 (5)	P(2)-Cr-C(1)	91.13 (19)
P(1)-Cr-P(3)	95.26 (5)	P(2)-Cr-C(2)	85.02 (17)
P(2)-Cr-P(3)	99.43 (5)	P(3)-Cr-C(2)	90.72 (17)
P(1)-Cr-C(2)	173.86 (17)	P(3)-Cr-C(3)	85.42 (18)
P(2)-Cr-C(3)	173.04 (18)	C(1)-Cr-C(2)	86.83 (25)
P(3)-Cr-C(1)	168.92 (19)	C(1)-Cr-C(3)	83.77 (25)
P(1)-Cr-C(1)	87.56 (19)	C(2)-Cr-C(3)	89.95 (24)
P(1)-Cr-C(3)	91.91 (18)		
(b) Metal-Carbon-Oxygen Angles			
Cr-C(1)-O(1)	173.7 (5)	Cr-C(3)-O(3)	175.4 (5)
Cr-C(2)-O(2)	176.6 (5)		
(c) Metal-Phosphorus-Carbon Angles			
Cr-P(1)-C(11)	113.6 (2)	Cr-P(2)-C(25)	112.8 (2)
Cr-P(1)-C(13)	119.2 (2)	Cr-P(3)-C(31)	123.7 (2)
Cr-P(1)-C(15)	114.6 (2)	Cr-P(3)-C(33)	112.4 (2)
Cr-P(2)-C(21)	121.0 (2)	Cr-P(3)-C(35)	113.2 (2)
Cr-P(2)-C(23)	118.3 (2)		
(d) Phosphorus-Carbon-Carbon Angles			
P(1)-C(11)-C(12)	119.3 (5)	P(2)-C(25)-C(26)	115.0 (5)
P(1)-C(13)-C(14)	121.7 (5)	P(3)-C(31)-C(32)	120.1 (4)
P(1)-C(15)-C(16)	114.0 (4)	P(3)-C(33)-C(34)	118.5 (5)
P(2)-C(21)-C(22)	119.1 (5)	P(3)-C(35)-C(36)	115.3 (5)
P(2)-C(23)-C(24)	116.9 (5)		

$(PEt_3)_3$ as shown by the infrared spectrum (ν(C–O) 1920 (s), 1820 (s) cm^{-1}).[11] Slow cooling of the toluene solution to −50 °C yielded yellow crystals, suitable for X-ray diffraction studies. All reactions were carried out under an inert atmosphere. Preliminary data suggest that one of the other products of this reaction is an exceedingly air-sensitive mixed-metal cluster.

Collection of X-ray Diffraction Data. A fragment of size 0.3 × 0.3 × 0.2 mm was cleaved from a larger crystal and jam-fit into a 0.3-mm thin-walled capillary. The crystal was then mounted on a Syntex $P2_1$ diffractometer. Crystal alignment, determination of cell dimensions (monoclinic, with absences $0k0$ for $k = 2n + 1$), and data collection were accomplished as described previously.[12] Details appear in Table I.

Solution and Refinement of the Structure. All calculations were performed with the Syntex XTL system. Data were corrected for Lorentz and polarization factors; no correction for absorption was necessary ($\mu(\Delta t) \simeq 0.06$). Data were placed on an approximate absolute scale via a Wilson plot. A three-dimensional Patterson synthesis yielded the positions of the CrP_3 unit and suggested that the true space group was $P2_1$ (rather than $P2_1/m$). The remaining nonhydrogen atoms were located from a difference-Fourier synthesis, and all hydrogen atoms were input in calculated positions (d(C–H) = 0.95 Å,[13] idealized tetrahedral geometry, with methyl groups defined in the perfectly staggered conformation). Refinement converged with $R_F = 3.1\%$, $R_{wF} = 3.7\%$, and GOF = 1.715 for those 1761 reflections with $|F_o| > 3\sigma(|F_o|)$. The secondary extinction parameter, g, had a value of 2.8×10^{-8} (see eq 1). A final difference-Fourier synthesis

$$F_o^{cor} = (1.0 + gI_o)(F_o^{uncor}) \qquad (1)$$

had a peak of height 0.22 e $Å^{-3}$ as its largest feature. Refinement with inverted coordinates produced higher discrepancy indices, so the chirality of the acentric crystal was initially correctly defined.

Final atomic positional and thermal parameters are collected in Tables II and III.

Discussion

The molecular structure is shown in Figures 1 (labeling diagram) and 2 (stereoscopic view). The arrangement of ligands about the central Cr(0) atom is significantly distorted from the idealized octahedral geometry. The OC–Cr–CO angles are C(1)–Cr–C(3) = 83.77 (25)°, C(1)–Cr–C(2) = 86.83 (25)°, and C(2)–Cr–C(3) = 89.95 (24)°. The average value of 86.85° is substantially lower than OC–M–CO angles determined in other species, viz., 90.5° in the {*cis*-$Mn(CO)_2[P(OMe)_2Ph]_4^+$} cation,[3] 90.0° in *fac*-$Mn(CO)_3[P(OMe)_2Ph]_2Br$,[14] 89.6° in $W(CO)_5[P(t\text{-}Bu)_3]$,[2] 89.4° in $Mn(CO)_4(PPh_3)Cl$,[15] and 89.3° in $Cr(CO)_2(PH_3)_4$.[5]

The Cr–P bond lengths in the present complex—Cr–P(1) = 2.420 (2), Cr–P (2) = 2.432 (2), Cr–P (3) = 2.435 (2) Å

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Table VI. Bond Distances (Å) for Selected Phosphine and Phosphite Derivatives of $Cr(CO)_6$

complex	Cr–P	Cr–CO(trans)	C–O(trans)	Cr–CO(cis)	C–O(cis)
fac-$Cr(CO)_3(PEt_3)_3$	2.429 [8]	1.829 [8]	1.162 [3]		
$Cr(CO)_5(PPh_3)$[1]	2.422 (1)	1.845 (4)	1.154 (5)	1.880 [11]	1.150 [5]
cis-$Cr(CO)_4(PH_3)_2$[16]	2.349 (2)	1.847 (4)	1.162 (6)	1.914 (7)	1.113 (33)
fac-$Cr(CO)_3(PH_3)_3$[4]	2.346 (4)	1.84 (1)	1.16 (1)		
cis-$Cr(CO)_2(PH_3)_4$[5]	2.338 (4)[a] 2.282 (4)[b]	1.817 (7)			
$Cr(CO)_5[P(OPh)_3]$[1]	2.309 (1)	1.861 (4)	1.136 (6)	1.896 [6]	1.131 [3]
trans-$Cr(CO)_4[P(OPh)_3]_2$[17]	2.252 (1)			1.878 [4]	1.140 [6]

[a] Trans to CO. [b] Trans to another phosphine ligand.

[average = 2.429 [8] Å]—represent the longest chromium(0)–phosphorus bonds characterized to date (see Table VI). Of particular interest is a comparison with the closely related species *fac*-$Cr(CO)_3(PH_3)_3$,[4] in which the Cr–P distances average 2.346 (4) Å. The longer Cr–P distances in *fac*-$Cr(CO)_3(PEt_3)_3$ suggest a weakening of the Cr–P bonds caused by steric interactions between the adjacent PEt_3 ligands.

The short Cr–CO bond lengths [1.829 [8] Å (average)] and long C–O bond lengths [1.162 [3] Å (average)] in *fac*-$Cr(CO)_3(PEt_3)_3$ are consistent with strong d_π–π^*(CO) back-donation and suggest that PEt_3 behaves essentially as a σ-donor ligand, with little or no π-acceptor capability.

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Registry No. *fac*-$Cr(CO)_3(PEt_3)_3$, 73505-52-9; $Na^+[Mn(CO)_5^-]$, 13859-41-1.

Supplementary Material Available: Tables of structure factors and data processing formulas (10 pages). Ordering information is given on any current masthead page.

Correspondence

Effects of Planar and Tetrahedral Distortions on the ESR Parameters of Bis(salicylaldiminato)copper(II) Complexes

Sir:

Many papers have been dealing with pseudotetrahedral copper(II) complexes[1–4] and much is known on the ESR parameters of such compounds as well as of similar chromophores present in naturally occurring compounds like the blue proteins.[5,6] In order to avoid exchange narrowing effects which might wash out any hyperfine interaction, researchers often have diluted the paramagnetic complexes into diamagnetic host lattices. The host lattice, however, may induce some changes on the geometry of the guest complex with respect to the geometry of the pure paramagnetic complex.[7] This is well-known to happen for example for the complex bis(*N*-methylsalicylaldiminato)copper(II) which is planar when pure but is able to undertake the dimeric five-coordinate structure of the host zinc(II) complex.[8]

In order to better understand the effects of a pseudotetrahedral distortion upon a planar chromophore with respect to the ESR parameters, we studied a series of bis(*N*-alkylsalicylaldiminato)copper(II) complexes.

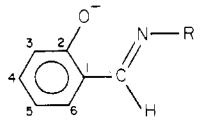

Table I. ESR Data of Some Bis(salicylaldiminato)copper(II) Complexes

compd	$g_\parallel$	$g_\perp$	$A_\parallel$[a]	$A_\perp$[a]	g_0	A_0[a]
(Cu,Zn)-5-Me-Sal-*i*-Pr	2.27	2.03–2.11	113			
(Cu,Pd)-5-Me-Sal-*i*-Pr	2.22	2.04	186			
(Cu,Zn)-3-Me-Sal-*i*-Pr	2.27	2.03–2.11	120			
(Cu,Pd)-3-Me-Sal-*i*-Pr	2.22	2.05	186			
(Cu,Ni)Sal-Et	2.22	2.05	194			
(Cu,Pd)Sal-Et	2.22	2.05	194			
(Cu,Ni)Sal-*n*-Pr	2.22	2.05	190			
(Cu,Pd)Sal-*n*-Pr	2.21	2.05	190			
(Cu,Ni)Sal-NH[b]	2.20	2.05	185			
(Cu,Ni)Sal-NMe[c]	2.21	2.04–2.06	186	21		
CuSal-NMe[d]	2.22	2.05	195		2.109	76
(Cu,Zn)Sal-*i*-Pr[e]	2.28	2.095–2.014	117	≃30, ≃15		
(Cu,Zn)Sal-*t*-Bu[f]	2.29	2.08–2.03	117	≃20, ≃12		
CuSal-*t*-Bu[d]	2.27	2.07	145	≃8	2.135	43

[a] $cm^{-1} \times 10^{-4}$. [b] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958). [c] M. A. Hitchman, C. D. Olson, and R. L. Belford, *ibid.*, **50**, 1195 (1968). [d] Glassy solutions in toluene, see ref 2. [e] H. P. Fritz, B. M. Golla, and H. J. Keller, *Z. Naturforsch.*, *B*, **21**, 1015 (1966). [f] H. P. Fritz, B. M. Golla, and H. J. Keller, *ibid.*, *B*, **23**, 876 (1968).

The geometry of the donor atoms around the copper(II) ion depends on the nature of the R group, the tetrahedral distortion increasing with the bulkiness of R.[9] The pure palladium complexes are planar whereas the pure zinc derivatives are pseudotetrahedral. Through slow evaporation of the chloroform–methanol solutions containing the bis(*N*-alkylsalicylaldiminato)zinc(II) or -palladium(II) complexes and 1% of the analogous copper(II) complex,[10] doped compounds have been obtained which show X-ray diffraction patterns equal to those of the host complexes. Through this procedure the compounds 5-CH_3-CuSal-*i*-Pr and 3-CH_3-CuSal-*i*-Pr have

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