

Isomerism in Nitrosyl-Isocyanide Complexes of Chromium of the Types [Cr(NO)(CNR)₃(L-L)]ⁿ⁺ and [Cr(NO)(CNR)₄(L)]ⁿ⁺

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The reactions of the chelating ligands bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos) with nitrosyl-isocyanide complexes of chromium [Cr(NO)(CNR)₃]PF₆ (R = CMe₃ or Me) in refluxing 1-propanol lead to the formation of the series *mer*-[Cr(NO)(CNR)₃(L-L)]PF₆. Similar reactions of [Cr(NO)(CNR)₃]PF₆ with the monodentate phosphines PEtPh₂, PPh₃, and 2-(diphenylphosphino)pyridine (Ph₂Ppy) allow the isolation of *cis*-[Cr(NO)(CNR)₄(L)]PF₆ (for R = CMe₃). Cyclic voltammetric studies of these 18-electron, formally Cr(0) complexes show that they exhibit a one-electron oxidation at $E_{1/2} \approx +0.4$ V vs. SCE. Chemical oxidation of these compounds in acetone using NOPF₆ affords the corresponding 17-electron Cr(I) derivatives *mer*-[Cr(NO)(CNR)₃(L-L)](PF₆)₂ and *cis*-[Cr(NO)(CNR)₄(L)](PF₆)₂ (in the latter case for R = CMe₃ and L = PPh₃). The complexes *mer*-[Cr(NO)(CNR)₃(L-L)]PF₆ are observed to undergo a slow isomerization to the corresponding *fac* isomers upon their oxidation, a process that can be conveniently followed by ESR spectroscopy. These isomerizations may occur by a nondissociative, trigonal-twist mechanism in the L-L = dppe or arphos series and a dissociative mechanism for the L-L = dppm complexes, as suggested by various ESR spectral measurements. An X-ray crystal structure determination of *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]PF₆ confirms the geometry of this isomer. The compound crystallizes in space group $P2_1/c$ (No. 19) with $a = 26.742$ (4) Å, $b = 16.591$ (2) Å, $c = 22.440$ (4) Å, $\beta = 115.10$ (1)°, and $Z = 8$ (two formula units per asymmetric unit). Least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with mixed isotropic and anisotropic temperature factors and 4866 unique reflections with $F_o > 5\sigma(F_o)$ collected on an Enraf-Nonius CAD-4 diffractometer gave an R of 0.082. Although large thermal motions in the PF₆ groups and in one of the CNCMe₃ groups in each molecule limit the precision of the determination, it is apparent that the NO group has a larger structural trans effect than the CNCMe₃ group [Cr-P averages 2.478 (2) Å trans to NO and 2.347 (2) Å trans to CNCMe₃]. The Cr-N distances average 1.71 (1) Å, the Cr-C distances, 1.96 (1) Å, and the Cr-N-O angles, 178.2 (8)°; the Cr-C-N angles range from 172.7 (8) to 178.8 (7)°.

Introduction

In exploring the reaction chemistry of the nitrosyl-pentakis(isocyanide) complexes [Cr(NO)(CNR)₅]X (R = CMe₃, CHMe₂, or Me; X = PF₆ or BF₄)^{1,2} toward trialkylphosphines (PEt₃, P-*n*-Pr₃, or P-*n*-Bu₃) or dialkylphenylphosphines (PMe₂Ph or PEt₂Ph), we isolated the complexes *trans*-[Cr(NO)(CNR)₄(PR₃)]X.³ Similarly, when the reaction of the bidentate chelating phosphine 1,2-bis(diphenylphosphino)ethane (dppe) with [Cr(NO)(CNCMe₃)₃]PF₆ was carried out in refluxing ethanol, then the substitution product *fac*-[Cr(NO)(CNR)₃(dppe)]PF₆ was formed.³

In view of the reported syntheses of several related nitrosyl carbonyls of the type [M(NO)(CO)₃(L-L)]⁺⁴⁻⁷ (M = Cr, Mo, or W; L-L = bidentate nitrogen, phosphorus, or arsenic donor ligand), and in particular the differences often observed in the structures of these complexes,^{4,5,7} we have examined in detail the reactivities of the compounds [Cr(NO)(CNR)₃]PF₆ with bidentate ligands in order to establish which chelate derivatives and which isomers could be isolated. We have succeeded in synthesizing a series of chelating phosphine derivatives of the type *mer*-[Cr(NO)(CNR)₃(L-L)](PF₆)_n as well as the monodentate phosphine complexes *cis*-[Cr(NO)(CNR)₄(PR₃)](PF₆)_n ($n = 1$ or 2) in the case of PR₃ = PEtPh₂, PPh₃, and Ph₂Ppy. During the course of these studies in which we investigated the redox chemistry of these compounds, we have discovered that the chelate complexes undergo a *mer* → *fac* isomerization upon oxidation to their 17-electron congeners. These results have an important bearing upon the general phenomenon of electron-transfer-initiated isomerization changes, as exemplified by several such studies on substituted six-coordinate molybdenum carbonyl species.⁸⁻¹² Few such in-

vestigations have yet been carried out on analogous isocyanide complexes.¹³

The present report provides details of the syntheses of these complexes and structural assignments based upon the IR spectra and the ESR spectra of the 17-electron species. In addition, we have undertaken an X-ray structural study of the 18-electron compound *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]PF₆, the results of which are provided herein.

Experimental Section

Starting Materials. The nitrosyl-isocyanide complexes [Cr(NO)(CNCMe₃)₃]PF₆¹ and [Cr(NO)(CNMe)₃]PF₆¹⁴ were prepared according to literature procedures. The phosphine ligand 2-(diphenylphosphino)pyridine (abbreviated Ph₂Ppy) was prepared by the method developed in this laboratory,¹⁵ which is a modification of the procedure used by others.¹⁶ Other monodentate phosphines and the bidentate phosphine ligands bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos), as well as nitrosium hexafluorophosphate and all other reagents and solvents, were obtained from commercial sources and were used as received.

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen, and all solvents were deoxygenated prior to use by purging with N₂ gas.

A. Reactions of [Cr(NO)(CNR)₃]PF₆ (R = CMe₃ or Me) with Chelating Phosphine Ligands. (i) *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]PF₆. A quantity of [Cr(NO)(CNCMe₃)₃]PF₆ (0.125 g, 0.19 mmol) and excess dppm (0.18 g, 0.47 mmol) were stirred in 9 mL of 1-propanol and heated to reflux. After a reaction time of 2 h, the reaction mixture was stored at -10 °C for a period of 2 h. The red solid that had precipitated was filtered off, washed with diethyl ether, and dried in vacuo. The filtrate could be reduced in volume to precipitate an additional quantity of product, which was filtered off, washed with a small portion of ethanol (to remove unreacted starting material) followed by diethyl ether, and

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dried in vacuo; total yield 0.053 g (32%). This compound was recrystallized from dichloromethane–diethyl ether mixtures. Anal. Calcd for $C_{40}H_{49}CrF_6N_4OP_3$: C, 55.82; H, 5.74. Found: C, 55.19; H, 5.50.

(ii) *mer*-[Cr(NO)(CNCMe₃)₃(dpe)]PF₆. A mixture of [Cr(NO)(CNCMe₃)₃]PF₆ (0.15 g) and dpe (0.093 g) was stirred in 10 mL of 1-propanol at reflux. After 5 h, the reaction solution was allowed to cool slowly by packing the flask in a container of vermiculite and refrigerating it overnight. The red solid that formed was filtered off, washed with copious amounts of diethyl ether, and dried in vacuo. Recrystallization could be effected from dichloromethane–diethyl ether mixtures; yield 0.099 g (48%). Anal. Calcd for $C_{41}H_{51}CrF_6N_4OP_3$: C, 56.29; H, 5.88. Found: C, 55.79; H, 6.16.

(iii) *mer*-[Cr(NO)(CNCMe₃)₃(arphos)]PF₆. Red crystals of this complex were prepared in 48% yield by the method described in section A(i). Anal. Calcd for $C_{41}H_{51}AsCrF_6N_4OP_2$: C, 53.60; H, 5.60. Found: C, 54.02; H, 5.83.

(iv) *mer*-[Cr(NO)(CNMe)₃(dppm)]PF₆. A mixture of [Cr(NO)(CNMe)₃]PF₆ (0.125 g, 0.29 mmol) and excess dppm (0.28 g, 0.73 mmol) was stirred in 40 mL of refluxing 1-propanol. After a reaction time of 6 h, the mixture was cooled to near room temperature and the bright red crystals that formed were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.164 g (77%). Anal. Calcd for $C_{31}H_{31}CrF_6N_4OP_3$: C, 50.69; H, 4.25. Found: C, 50.45; H, 4.50.

(v) *mer*-[Cr(NO)(CNMe)₃(dpe)]PF₆. This compound was isolated as red crystals by a procedure analogous to that described in section A(ii); yield 84%. Anal. Calcd for $C_{32}H_{33}CrF_6N_4OP_3$: C, 51.34; H, 4.44. Found: C, 50.82; H, 4.63.

B. Oxidations of [Cr(NO)(CNR)₃(L–L)]PF₆ Complexes. (i) *mer*-[Cr(NO)(CNCMe₃)₃(dppm)](PF₆)₂. Solid NOPF₆ (0.052 g, 0.30 mmol) was added directly to a solution of *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]PF₆ (0.127 g, 0.15 mmol) in 5 mL of acetone. The resulting orange solution was filtered, and diethyl ether was added to the filtrate to precipitate bright yellow crystals of product. The crystals were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.114 g (66%). Anal. Calcd for $C_{40}H_{49}CrF_{12}N_4OP_4$: C, 47.77; H, 4.91. Found: C, 47.45; H, 5.07.

The following complexes were prepared by using essentially the same procedure as that described in section B(i).

(ii) *mer*-[Cr(NO)(CNCMe₃)₃(dpe)](PF₆)₂. Yield 64%. Anal. Calcd for $C_{41}H_{51}CrF_{12}N_4OP_4$: C, 48.29; H, 5.04. Found: C, 48.71; H, 5.66.

(iii) *mer*-[Cr(NO)(CNMe)₃(arphos)](PF₆)₂. Yield 69%. Anal. Calcd for $C_{41}H_{51}AsCrF_{12}N_4OP_3$: C, 46.30; H, 4.83. Found: C, 46.05; H, 5.10.

(iv) *mer*-[Cr(NO)(CNMe)₃(dppm)](PF₆)₂. Yield 75%. Anal. Calcd for $C_{31}H_{31}CrF_{12}N_4OP_4$: C, 42.34; H, 3.55. Found: C, 41.87; H, 3.82.

C. Formation of Derivatives with Monodentate Phosphines. (i) *cis*-[Cr(NO)(CNCMe₃)₄(PPh₂py)]PF₆. A mixture of [Cr(NO)(CNCMe₃)₃]PF₆ (0.175 g, 0.27 mmol) and 2-(diphenylphosphino)pyridine, (PPh₂py) (0.194 g, 0.74 mmol) was stirred in 10 mL of refluxing 1-propanol for 7 h. After this reaction period, the solution was allowed to cool slowly by placing the flask in a container of vermiculite and refrigerating it for several days. The red solid that precipitated was filtered off, washed with ethanol to remove unreacted starting complex, washed with diethyl ether, and dried in vacuo; yield 0.050 g (22%). Anal. Calcd for $C_{37}H_{50}CrF_6N_6OP_2$: C, 54.01; H, 6.12. Found: C, 54.47; H, 6.59.

The two following complexes were prepared by using procedures very similar to that described in section C(i).

(ii) *cis*-[Cr(NO)(CNCMe₃)₄(PPh₃)]PF₆. Yield 41%. The identity of this compound was established on the basis of its spectroscopic and electrochemical properties.

(iii) *cis*-[Cr(NO)(CNCMe₃)₄(PETPh₃)]PF₆. Yield 40%. Anal. Calcd for $C_{34}H_{51}CrF_6N_3OP_2$: C, 52.78; H, 6.64. Found: C, 52.83; H, 6.73.

D. Oxidation of *cis*-[Cr(NO)(CNCMe₃)₄(PPh₃)]PF₆. Oxidation of the title complex using NOPF₆, according to the procedure outlined in section B(i), afforded red-orange crystals of *cis*-[Cr(NO)(CNCMe₃)₄(PPh₃)](PF₆)₂ in 86% yield. Anal. Calcd for $C_{38}H_{51}CrF_{12}N_3OP_3$: C, 47.21; H, 5.32. Found: C, 47.26; H, 5.68.

X-ray Crystallography. Crystals of *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]PF₆ were grown by dissolving the crude reaction product in dichloromethane, adding diethyl ether, and allowing the solution to stand undisturbed for several days. Details of the solution and refinement and the complete structural parameters are available as supplementary material. A drawing of the [Cr(NO)(CNCMe₃)₃(dppm)]⁺ cation is shown in Figure 1. Atomic positions are listed in Table I, while the more important bond distances and angles are given in Table II. The compound crystallizes with two formula units per asymmetric unit; thus, we have two measurements of each distance. Full tables of thermal parameters and structure factors are available as supplementary material.

Physical Measurements. Infrared spectra of Nujol mulls were recorded in the region 4000–400 cm⁻¹ on KBr plates with an IBM In-

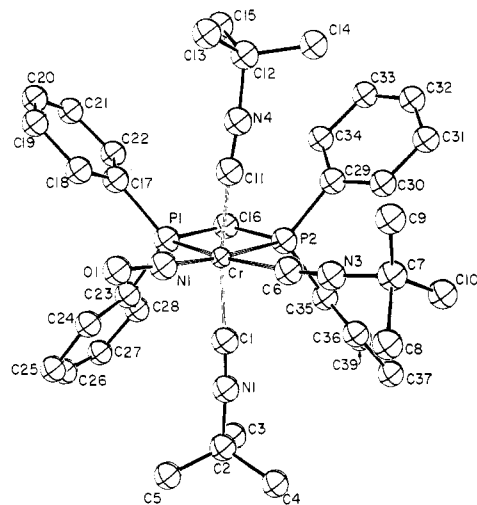


Figure 1. Structure of the *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]⁺ cations with isotropic temperature factors of arbitrary size. The phenyl ring carbon atom C40 is obscured by C35; C38 is obscured by C37. To match the atoms in the cations to those in Table I, place a 1 before the number of an atom in cation 1 and a 2 before an atom in cation 2. For example, P2 and C23 in cation 1 are P12 and C123 and in cation 2 they are P22 and C223.

struments IR/32 FTIR spectrometer. All other spectroscopic and electrochemical studies were carried out as described previously.¹ Dr. H. D. Lee of the Purdue University microanalytical laboratory performed the microanalyses.

Results and Discussion

Synthetic and Reactivity Studies. Reactions of the chelating phosphine ligands bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dpe), or 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos) with nitrosyl–isocyanide complexes of chromium [Cr(NO)(CNR)₃]PF₆ (R = CMe₃ or Me) in refluxing 1-propanol for periods of 6 h or less lead to the formation of the substitution products *mer*-[Cr(NO)(CNR)₃(L–L)]PF₆. The air-stable, red crystalline complexes are soluble in polar organic solvents, such as acetone and dichloromethane, and insoluble in diethyl ether and cold alcohol solvents. These 18-electron species serve as synthetic precursors to the analogous 17-electron compounds *mer*-[Cr(NO)(CNR)₃(L–L)](PF₆)₂, upon oxidation with solid NOPF₆.¹⁷ These reactions, which are accompanied by NO(g) evolution, occur rapidly in acetone solution to yield the air-stable, yellow crystalline compounds. The dicationic species [Cr(NO)(CNR)₃(L–L)]²⁺ can be reduced back to their 1+ congeners by treatment with Zn metal.

These results are especially noteworthy since in a previous study³ of the reaction between [Cr(NO)(CNCMe₃)₃]PF₆ and dpe in ethanol as solvent, it was the *fac* isomer of [Cr(NO)(CNCMe₃)₃(dpe)]PF₆ that had been isolated. We should perhaps consider this meridional series, which presumably forms following loss of the trans RNC ligand of [Cr(NO)(CNR)₃]PF₆,^{1,3} as the kinetic product. The formation of *fac*-[Cr(NO)(CNCMe₃)₃(dpe)]PF₆ probably resulted from the synthetic and workup procedures that were originally used,³ which required that the reaction product remain in solution over a period of several days, thereby allowing isomerization to the facial isomer to occur. This notion is supported by an IR spectral analysis of the red oil

(17) Certain related compounds of the group 6 metals,²⁸ in particular various nitrosyl carbonyls, have been synthesized by the reactions of NOPF₆ or NOBF₄ with M(CO)₄(L–L) precursors. These compounds include Connor's series *fac*-[M(NO)(CO)₃(L–L)]PF₆ [M = Cr, Mo, or W; L–L = 1,2-bis(dicyclohexylphosphino)ethane or 1,2-bis(dimethylphosphino)ethane],⁴ as well as the related 17-electron acetonitrile complexes *fac*-[Cr(NO)(NCMe)₃(L–L)](PF₆)₂.⁴ Connelly and co-workers have described the compounds *mer*-[Cr(NO)(CO)₃(dppm)]BF₄,⁵ [M(NO)(CO)₃(dppm)]PF₆ (M = Mo or W),⁶ *fac*-[Mo(NO)(CO)₃(L–L)]BF₄ (L–L = bpy or phen),⁷ and *mer*-[W(NO)(CO)₃(phen)]PF₆.⁷

Table I. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	atom	x	y	z
Cr1	0.12935 (8)	0.3804 (1)	0.76997 (9)	N24	0.4812 (4)	0.6107 (6)	0.1704 (5)
P11	0.8651 (1)	0.7091 (2)	0.3079 (2)	C21	0.2859 (4)	0.6891 (7)	0.1262 (5)
P12	0.8928 (1)	0.7581 (2)	0.2076 (2)	C22	0.1934 (5)	0.7712 (7)	0.1025 (6)
O11	0.8388 (3)	0.4766 (6)	0.2783 (5)	C23	0.8110 (5)	0.2829 (9)	0.3310 (6)
N11	0.8525 (4)	0.5347 (6)	0.2579 (5)	C24	0.7979 (5)	0.3535 (8)	0.4261 (8)
N12	-0.0046 (4)	0.6008 (6)	0.3182 (5)	C25	0.1457 (5)	0.7260 (8)	0.0513 (7)
N13	0.8859 (4)	0.5475 (6)	0.1105 (5)	C26	0.3634 (5)	0.5898 (7)	0.2217 (6)
N14	0.7505 (4)	0.6575 (6)	0.1275 (5)	C27	0.3654 (7)	0.54186 (9)	0.3275 (6)
C11	0.9486 (4)	0.6093 (7)	0.2848 (6)	C28	0.3414 (8)	0.571 (1)	0.3554 (8)
C12	0.0561 (5)	0.599 (1)	0.3656 (7)	C29	0.425 (1)	0.496 (2)	0.3680 (9)
C13	0.0715 (6)	0.688 (1)	0.3865 (8)	C210	0.343 (1)	0.445 (1)	0.313 (1)
C14	0.0856 (6)	0.567 (1)	0.3245 (8)	C211	0.4360 (5)	0.6207 (7)	0.1614 (6)
C15	0.0617 (8)	0.541 (1)	0.421 (1)	C212	0.5395 (5)	0.6022 (9)	0.1798 (7)
C16	0.8810 (5)	0.5731 (7)	0.1558 (6)	C213	0.5737 (5)	0.5843 (9)	0.2548 (7)
C17	0.8900 (6)	0.5179 (9)	0.0480 (6)	C214	0.5556 (5)	0.686 (1)	0.1610 (7)
C18	0.9246 (7)	0.436 (1)	0.0678 (9)	C215	0.5406 (5)	0.533 (1)	0.1366 (7)
C19	0.1708 (7)	0.505 (1)	-0.0010 (8)	C216	0.6343 (4)	0.3277 (7)	0.3943 (5)
C110	0.9197 (8)	0.578 (1)	0.0292 (8)	C217	0.7067 (4)	0.2493 (8)	0.5186 (6)
C111	0.7955 (5)	0.6442 (7)	0.1669 (6)	C218	0.7396 (5)	0.3185 (8)	0.0449 (6)
C112	0.6948 (5)	0.6764 (8)	0.0804 (6)	C219	0.7859 (6)	0.3119 (9)	0.1070 (7)
C113	0.6613 (6)	0.5963 (9)	0.0742 (8)	C220	0.2029 (5)	0.7351 (8)	0.3608 (7)
C114	0.6994 (6)	0.694 (1)	0.0152 (7)	C221	0.2347 (5)	0.6685 (8)	0.3887 (7)
C115	0.3249 (6)	0.249 (1)	0.3912 (8)	C222	0.2827 (5)	0.6756 (8)	0.4521 (6)
C116	0.1232 (5)	0.3027 (8)	0.2266 (6)	C223	0.5916 (5)	0.2308 (8)	0.4765 (6)
C117	0.1999 (5)	0.2241 (8)	0.1804 (6)	C224	0.5611 (6)	0.3010 (9)	0.4748 (7)
C118	0.7718 (6)	0.6533 (9)	0.3180 (7)	C225	0.5220 (7)	0.295 (1)	0.5047 (8)
C119	0.7221 (7)	0.662 (1)	0.3322 (9)	C226	0.5186 (6)	0.274 (1)	0.0295 (8)
C120	0.2926 (6)	0.237 (1)	0.1551 (8)	C227	0.5472 (6)	0.347 (1)	0.0335 (8)
C121	0.2621 (7)	0.305 (1)	0.1517 (9)	C228	0.5859 (6)	0.3453 (9)	-0.0008 (7)
C122	0.2107 (6)	0.3034 (9)	0.1646 (7)	C229	0.5388 (4)	0.3078 (7)	0.2626 (5)
C123	0.855 (5)	0.2057 (8)	0.1064 (6)	C230	0.5084 (5)	0.2591 (8)	0.2087 (6)
C124	0.9212 (6)	0.631 (1)	0.4211 (8)	C231	0.4544 (5)	0.2862 (8)	0.1653 (7)
C125	0.0392 (8)	0.377 (1)	0.507 (1)	C232	0.4338 (5)	0.3574 (8)	0.1785 (6)
C126	0.0156 (7)	0.308 (1)	0.4789 (8)	C233	0.4629 (5)	0.4034 (8)	0.2320 (7)
C127	0.9864 (7)	0.743 (1)	-0.0020 (9)	C234	0.5186 (5)	0.3808 (8)	0.2768 (6)
C128	0.0530 (6)	0.274 (1)	0.0744 (8)	C235	0.6544 (4)	0.3307 (7)	0.2684 (5)
C129	0.1499 (5)	0.3129 (7)	0.3685 (6)	C236	0.6506 (5)	0.2861 (8)	0.2185 (6)
C130	0.1447 (7)	0.285 (1)	0.4251 (8)	C237	0.6758 (6)	0.3227 (9)	0.1785 (7)
C131	0.8238 (7)	0.671 (1)	0.5121 (9)	C238	0.6947 (5)	0.4008 (8)	0.1933 (7)
C132	0.7935 (7)	0.608 (1)	0.5148 (8)	C239	0.6899 (5)	0.4463 (8)	0.2437 (6)
C133	0.2151 (7)	0.414 (1)	0.4377 (8)	C240	0.6634 (5)	0.4093 (8)	0.2821 (6)
C134	0.1838 (6)	0.3773 (9)	0.3691 (7)	P3	0.6068 (2)	0.5622 (2)	0.4483 (2)
C135	0.0375 (5)	0.2897 (7)	0.2789 (6)	P4	0.1197 (2)	0.5362 (3)	0.1701 (2)
C136	0.9918 (5)	0.7375 (8)	0.1987 (6)	F1	0.6127 (8)	0.5174 (6)	0.3958 (5)
C137	0.9555 (5)	0.2618 (8)	0.2969 (7)	F2	0.6371 (4)	0.6298 (6)	0.4322 (5)
C138	0.9353 (5)	0.3390 (9)	0.2707 (6)	F3	0.6558 (5)	0.534 (1)	0.5018 (6)
C139	0.9631 (6)	0.3890 (9)	0.2467 (7)	F4	0.5901 (5)	0.6037 (8)	0.4950 (5)
C140	0.0191 (5)	0.3663 (8)	0.2512 (7)	F5	0.5730 (5)	0.4917 (7)	0.4553 (7)
Cr2	0.35756 (7)	0.8562 (1)	0.63925 (9)	F6	0.5541 (5)	0.6046 (8)	0.3963 (8)
P21	0.3556 (1)	0.7342 (2)	0.0578 (2)	F7	0.0661 (5)	0.5247 (9)	0.1813 (5)
P22	0.6111 (1)	0.2791 (2)	0.3126 (2)	F8	0.1339 (4)	0.6139 (5)	0.2114 (5)
O21	0.3183 (4)	0.5027 (6)	0.0582 (5)	F9	0.1494 (6)	0.4917 (6)	0.2341 (5)
N21	0.3340 (4)	0.5604 (6)	0.0918 (5)	F10	0.1081 (8)	0.4601 (6)	0.1310 (5)
N22	0.7550 (4)	0.2244 (6)	0.3830 (4)	F11	0.0850 (5)	0.5826 (6)	0.1054 (5)
N23	0.3663 (4)	0.5557 (6)	0.2667 (5)	F12	0.1701 (5)	0.5544 (7)	0.1533 (5)

that is initially obtained from our previous reaction procedure.³ An IR spectrum of a dichloromethane solution of this oil revealed the presence of the *mer* isomer only. Thus, for the complex $[\text{Cr}(\text{NO})(\text{CNCMe}_3)_3(\text{dppe})]\text{PF}_6$, and in all likelihood for the entire $[\text{Cr}(\text{NO})(\text{CNR})_3(\text{L-L})]\text{PF}_6$ series, we may consider the *mer* isomer as the kinetic product while the *fac* isomer, which forms only after several days in solution, is the thermodynamic product. This isomerization process will be discussed further following consideration of the electrochemical properties of these complexes.

The monodentate phosphines Ph_2Ppy , PPh_3 , and PEtPh_2 react with $[\text{Cr}(\text{NO})(\text{CNCMe}_3)_3]\text{PF}_6$ to form the monosubstituted products $\text{cis}-[\text{Cr}(\text{NO})(\text{CNCMe}_3)_4(\text{PR}_3)]\text{PF}_6$.¹⁸ The ligand 2-(diphenylphosphino)pyridine (Ph_2Ppy) has previously been observed to partake in various bonding modes;^{19,20} its inclusion in

the present study arose from our attempts to form a complex in which the ligand served as a chelate.¹⁹ However, spectroscopic and microanalytical data leave no doubt as to the monodentate, phosphorus-bound nature of this ligand in the complex $\text{cis}-[\text{Cr}(\text{NO})(\text{CNCMe}_3)_4(\text{PPh}_2\text{py})]\text{PF}_6$ (Table III). The 18-electron PPh_3 compound, like its chelating phosphine relatives, may be oxidized in acetone solution by NOPF_6 to form the red-orange, paramagnetic, 17-electron species $\text{cis}-[\text{Cr}(\text{NO})(\text{CNCMe}_3)_4(\text{PPh}_3)](\text{PF}_6)_2$.

The *cis* configuration observed in these compounds stands in contrast to the *trans*- $[\text{Cr}(\text{NO})(\text{CNR})_4(\text{PR}_3)]\text{PF}_6$ complexes isolated previously,³ where PR_3 is a trialkylphosphine or dialkylphenylphosphine ligand. As the presence of a *trans*-labilizing NO ligand might lead us to predict, the species *trans*- $[\text{Cr}$

(18) The choice of solvent for these reactions appears to be quite critical; 1-propanol is satisfactory whereas very little reaction occurs when 2-propanol is used, presumably because of its lower reflux temperature.

(19) Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.

(20) Farr, J. P.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 6654.

Table II. Selected Distances (Å) and Angles (deg) with Estimated Standard Deviations^a

dist	cation 1	cation 2	dist	cation 1	cation 2
Cr-P1	2.350 (2)	2.344 (2)	C11-N4	1.150 (8)	1.163 (8)
Cr-P2	2.478 (2)	2.477 (2)	N2-C2	1.490 (9)	1.495 (7)
Cr-N1	1.724 (7)	1.693 (7)	N3-C7	1.51 (1)	1.52 (1)
Cr-C1	1.947 (8)	1.961 (8)	N4-C12	1.466 (9)	1.50 (1)
Cr-C6	1.969 (8)	1.997 (8)	N1-C1	2.72 (1)	2.77 (1)
Cr-C11	1.956 (8)	1.954 (8)	N1-C6	2.80 (1)	2.72 (1)
N1-O1	1.179 (6)	1.188 (7)	N1-C11	2.69 (1)	2.70 (1)
C1-N2	1.158 (7)	1.163 (7)	C1-C6	2.77 (1)	2.80 (1)
C6-N3	1.145 (8)	1.111 (8)	C6-C11	2.71 (1)	2.85 (1)
angle	cation 1		cation 2		
P1-Cr-P2	70.25 (7)		69.82 (7)		
P1-Cr-N1	97.8 (2)		98.6 (2)		
P1-Cr-C1	88.7 (2)		86.5 (2)		
P1-Cr-C6	163.7 (2)		166.7 (2)		
P1-Cr-C11	91.7 (2)		89.3 (2)		
P2-Cr-N1	167.9 (2)		168.4 (2)		
P2-Cr-C1	86.2 (2)		81.2 (2)		
P2-Cr-C6	93.4 (2)		97.0 (2)		
P2-Cr-C11	85.5 (2)		86.4 (2)		
N1-Cr-C1	95.5 (3)		98.3 (3)		
N1-Cr-C6	98.6 (3)		94.6 (3)		
N1-Cr-C11	93.5 (3)		93.8 (3)		
C1-Cr-C6	89.9 (3)		90.1 (3)		
C1-Cr-C11	171.0 (3)		167.6 (3)		
C6-Cr-C11	87.3 (3)		91.3 (3)		
Cr-N1-O1	177.3 (6)		178.6 (7)		
C1-N2-C2	173.7 (6)		177.1 (7)		
C6-N3-C7	177.5 (8)		172.6 (9)		
C11-N4-C12	177.2 (7)		176.5 (8)		
Cr-C1-N2	178.8 (7)		172.6 (6)		
Cr-C6-N3	176.3 (7)		176.6 (7)		
Cr-C11-N4	177.0 (6)		175.1 (7)		

^a To match the atoms in the cations to those in Table I, place a 1 before the number of an atom in cation 1 and a 2 before an atom in cation 2. For example, P2 and C23 in cation 1 are P12 and C123 and in cation 2 they are P22 and C223.

(NO)(CNCMe₃)₄(PR₃)⁺ (PR₃ = PEtPh₂, PPh₃, or PPh₂py) are in all likelihood formed as intermediates (although we did not isolate or detect such species), but the final products we isolate, presumably the thermodynamic products, are the *cis* isomers. Simple electronic arguments suggest that a PR₃ ligand (a weaker π -acid than RNC) trans to the nitrosyl is the more favored configuration. The steric demands of the bulky alkylidiphosphine and triphenylphosphine, however, would have these ligands *cis* to the nitrosyl, and this particular effect apparently dictates the geometry.

Table III. Infrared Data, Voltammetric Half-Wave Potentials, and Molar Conductances of Nitrosyl-Isocyanide-Phosphine Complexes of Chromium

complex	$\nu(\text{NO})$, ^a cm ⁻¹	$\nu(\text{C}\equiv\text{N})$, ^a cm ⁻¹	$E_{1/2}$, ^b V	Λ_m ^c
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (dppm)]PF ₆	1645 s	2161 m, 2116 s, 2068 sh	+0.42 (85), ox	116
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (dppe)]PF ₆	1636 s	2155 m, 2113 s, 2062 sh	+0.39 (90), ox	120
<i>fac</i> -[Cr(NO)(CNCMe ₃) ₃ (dppe)]PF ₆	1659 s	2194 m, 2133 s, 2106 s	+0.32 (100), ox	120
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (arphos)]PF ₆	1637 s	2156 m, 2114 s, 2058 sh	+0.43 (90), ox	117
<i>mer</i> -[Cr(NO)(CNMe ₃) ₃ (dppm)]PF ₆	1655 s ^e	2186 m, 2146 s	+0.37 (110), ox	119
<i>mer</i> -[Cr(NO)(CNMe ₃) ₃ (dppe)]PF ₆	1650 s ^e	2182 m, 2141 s	+0.33 (115), ox	123
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (dppm)](PF ₆) ₂	1763 s	2205 s	+0.43 (105), red	262
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (dppe)](PF ₆) ₂	1778 s	2211 s	+0.38 (95), red	241
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (arphos)](PF ₆) ₂	1758 s	2209 s	+0.42 (95), red	261
<i>mer</i> -[Cr(NO)(CNMe ₃) ₃ (dppm)](PF ₆) ₂	1750 s	2248 m-s	+0.38 (110), red	257
<i>cis</i> -[Cr(NO)(CNCMe ₃) ₄ (PPh ₂ py)]PF ₆	1662 sh, 1651 s	2199 m, 2168 m, 2135 sh, 2114 s, 2070 sh	+0.34 (100), ox	121
<i>cis</i> -[Cr(NO)(CNCMe ₃) ₄ (PPh ₃)]PF ₆	1662 sh, 1651 s	2199 m, 2168 m, 2137 sh, 2113 s, 2075 sh	+0.36 (95), ox	130
<i>cis</i> -[Cr(NO)(CNCMe ₃) ₄ (PEtPh ₂)]PF ₆	1657 s	2203 m, 2159 m, 2115 s, 2067 sh	+0.33 (140), ox	121
<i>cis</i> -[Cr(NO)(CNCMe ₃) ₄ (PPh ₃)](PF ₆) ₂	1769 s	2226 sh, 2217 s	+0.38 (100), red	261

^a Nujol mull spectra. Abbreviations are as follows: s, strong; m, medium; sh, shoulder. ^b In volts vs. SCE with a Pt-bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. Measurements were carried out on dichloromethane solutions. Values of $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses. ^c Values in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, measured on $\sim 10^{-3}$ M acetonitrile solutions of complexes at room temperature. The complexes have conductivities typical of 1:1 or 1:2 electrolytes; see: Geary, W. J. *Coord. Chem. Rev.* 1971, 7, 81. ^d Data taken from ref 3. ^e Closely split doublet. The solution spectrum (in CH₂Cl₂) shows a single peak.

Crystal Structure of *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]PF₆. The crystal structure confirms the *mer* geometry of this complex (Figure 1). The compound crystallizes with a distorted-octahedral geometry about chromium consisting of a trans pair of CNCMe₃ ligands, an NO group trans to one phosphorus atom of the chelating dppm ligand, and a CNCMe₃ trans to the other phosphorus atom. The NO ligand exhibits a stronger structural trans effect than CNCMe₃, with the Cr-P distance trans to the NO averaging 0.130 Å longer than that trans to CNCMe₃; the averages are 2.478 (2) and 2.347 (2) Å, respectively. The other metal-ligand distances are unremarkable: the Cr-N distances average 1.708 (15) Å; the Cr-C distances, 1.964 (18) Å. The Cr-C-N and C-N-C linkages are close to linear; the Cr-C-N angles range from 172.7 (6) to 178.8 (7)°, and the C-N-C angles range from 172.2 (8) to 177.5 (8)°. The principal cause of the distortion from octahedral geometry appears to be the small bite angle of the dppm ligand (70.0 (1)° average) and the relatively short Cr-N and Cr-C distances. The resulting C-N repulsions within the coordination sphere give N-Cr-C angles ranging from 93.5 (3) to 98.6 (3)°.

Spectroscopic and Electrochemical Properties. Table III summarizes the IR spectra of Nujol mulls of the complexes prepared in this study. Of particular interest are the $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{NO})$ modes that occur in the regions 2250-2050 and 1800-1600 cm⁻¹, respectively. For the series [Cr(NO)(CNR)₃(L-L)]PF₆, three IR-active $\nu(\text{C}\equiv\text{N})$ bands are predicted (under *C_s* symmetry) for both the *fac* and the *mer* isomers. However, the assignment of these compounds as the *mer* isomers ultimately rests upon their spectroscopic similarity to the structurally characterized *mer*-[Cr(NO)(CNCMe₃)₃(dppm)]PF₆, a comparison with the $\nu(\text{C}\equiv\text{N})$ modes for *fac*-[Cr(NO)(CNCMe₃)₃(dppe)]PF₆³ (data for this complex are included in Table III), and the ESR spectral properties of the 17-electron dicationic analogues (*vide infra*). All three of the $\nu(\text{C}\equiv\text{N})$ modes are seen for the *tert*-butyl isocyanide derivatives; for *mer*-[Cr(NO)(CNCMe₃)₃(dppe)]PF₆, these are observed at lower energies than those in the IR spectrum of the corresponding *fac* complex (see ref 3). In the methyl isocyanide compounds, only two $\nu(\text{C}\equiv\text{N})$ modes are observed.

Upon oxidation of [Cr(NO)(CNR)₃(L-L)]PF₆ to their corresponding dicationic analogues, the IR spectra simplify considerably (Table III). Both the $\nu(\text{C}\equiv\text{N})$ and the $\nu(\text{NO})$ modes shift to higher energies, as the depopulation of the π^* levels of the ligands would lead us to predict, but in the 2+ compounds, only one $\nu(\text{C}\equiv\text{N})$ band is observed. The reasons for this spectral simplification are not fully known. However, as a similar effect is observed in the IR spectrum of the parent complex [Cr(NO)(CNCMe₃)₃]PF₆ upon its oxidation,¹ these observations are not unprecedented.

The very complex $\nu(\text{C}\equiv\text{N})$ region of the IR spectra of the compounds [Cr(NO)(CNCMe₃)₄(PR₃)]PF₆ (PR₃ = PEt₂Ph,

Table IV. X-Band ESR Data and Magnetic Moments of Nitrosyl-Isocyanide-Phosphine Complexes of Chromium

complex	g_{av}^a	$A(^{31}\text{P-cis}),$ G	$A(^{31}\text{P-trans}),$ G	$A(^{14}\text{N}),$ G	$A(^{53}\text{Cr}),$ G	$\mu_{obsd},^b$ μ_B
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (dppm)](PF ₆) ₂	1.9970	32.2	22.0	4.3	17.0	1.9
<i>fac</i> -[Cr(NO)(CNCMe ₃) ₃ (dppm)] ²⁺ ^c	1.9937	30.6		4.5	17.0	
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (dppe)](PF ₆) ₂	1.9962	30.0	20.5	4.4	17.1	1.8
<i>fac</i> -[Cr(NO)(CNCMe ₃) ₃ (dppe)] ²⁺ ^d	1.9953	30.7		4.5	17.1	
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (arphos)](PF ₆) ₂	1.9963	30.2	20.9 ^e	4.4	17.1	1.9
<i>mer</i> -[Cr(NO)(CNCMe ₃) ₃ (dppm)](PF ₆) ₂	1.9961	30.2	22.2	<i>f</i>	17.0	
<i>fac</i> -[Cr(NO)(CNMe) ₃ (dppm)] ²⁺ ^c	1.9934	30.4		<i>f</i>	17.3	
<i>mer</i> -[Cr(NO)(CNMe) ₃ (dppe)] ²⁺	1.9966	30.1	21.9	<i>f</i>	17.0	
<i>cis</i> -[Cr(NO)(CNCMe ₃) ₄ (PPh ₂ py)] ²⁺	1.9952	30.9		4.4	17.3	
<i>cis</i> -[Cr(NO)(CNCMe ₃) ₄ (PPh ₃)](PF ₆) ₂	1.9945	31.0		4.4	17.3	1.9
<i>cis</i> -[Cr(NO)(CNCMe ₃) ₄ (PEtPh ₂)] ²⁺	1.9950	31.4		4.5	17.3	

^a All samples run in CH₂Cl₂ solution at room temperature. If counterion is not specified, ESR spectrum was recorded on electrochemically generated sample. ^b Determined on dichloromethane solutions at room temperature by the Evans method. ^c Sample not isolated in the solid state; observed by ESR only. ^d Data from ref 3. ^e Coupling to ⁷⁵As ($I = 3/2$) in the trans (to the nitrosyl) position. ^f See text.

PPh₃, or PPh₂py), in conjunction with the ESR data of their 17-electron analogues (vide infra), unequivocally establish these complexes as the *cis* isomers. These IR spectral results contrast with the single, sharp $\nu(\text{C}\equiv\text{N})$ mode we observed in the spectra of *trans*-[Cr(NO)(CNR)₄(PR₃)]PF₆ (PR₃ = PEt₃, *P-n*-Pr₃, *P-n*-Bu₃, PMe₂Ph, or PEt₂Ph).³ Simplification in the $\nu(\text{C}\equiv\text{N})$ region of *cis*-[Cr(NO)(CNCMe₃)₄(PPh₃)₄(PPh₃)](PF₆)₂, relative to that of its 18-electron congener, is noted here as well, in addition to the expected shift to higher energies of both $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{NO})$ by $\sim 100\text{ cm}^{-1}$.

The electrochemical properties of complexes prepared in this study were investigated by using the cyclic voltammetry technique. Voltammetric half-wave potentials vs. SCE (in 0.2 M tetra-*n*-butylammonium hexafluorophosphate-dichloromethane) and $E_{p,a} - E_{p,c}$ values are reported in Table III. As in the case of the parent series [Cr(NO)(CNR)₃]^{*n*+}, and in related derivatives,^{1,3} each complex is characterized by a single wave in the CV (close to +0.4 V vs. SCE), representing the 17-electron/18-electron couple. Variable-scan rate studies performed on representative compounds are consistent with these being reversible electron-transfer processes.^{21,22} These electrochemical properties are in accord with the ease of oxidizing *mer*-[Cr(NO)(CNR)₃(L-L)]PF₆ to *mer*-[Cr(NO)(CNR)(L-L)](PF₆)₂ using NOPF₆.

Magnetic moment determinations were carried out at room temperature on dichloromethane solutions of the complexes by the Evans method (Table IV).²³ As expected, the monocationic Cr(0) complexes were diamagnetic, while the dicationic Cr(I) compounds exhibited values ($\mu_{obsd} \approx 1.5\ \mu_B$) consistent with these species possessing one unpaired electron.

Some details of the X-band ESR spectra of the 17-electron species *mer*-[Cr(NO)(CNR)₃(L-L)]²⁺ are given in Table IV. Observed *g* values occur in the range 1.99–2.00. In all cases, ligand hyperfine interaction of the unpaired spin with ³¹P nuclei provides evidence as to the structures of the complexes. The empirical difference we have observed³ in ³¹P *A* values for *cis* vs. *trans* coupling to the nitrosyl ligand [$A(^{31}\text{P}_{cis}) \approx 31\text{ G}$; $A(^{31}\text{P}_{trans}) \approx 21\text{ G}$] becomes paramount in this assignment.

In the compounds *mer*-[Cr(NO)(CNCMe₃)₃(L-L)]²⁺, where L-L is dppm or dppe, ligand hyperfine coupling occurs to two inequivalent ³¹P nuclei ($I = 1/2$), leading to a doublet of doublets. Such coupling can only occur from interaction with one equatorial and one axial phosphorus nucleus, and indeed the observed coupling constants are in accord with this assignment (Table IV). Therefore, these compounds are the *mer* isomers. Each of these lines is further split into 1:1:1 triplets by coupling to ¹⁴N ($I = 1$)

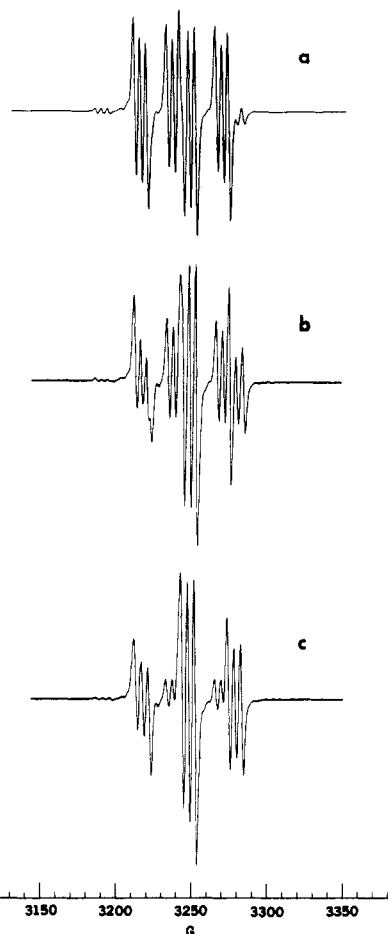


Figure 2. X-Band ESR spectra of a dichloromethane solution at room temperature containing *mer*-[Cr(NO)(CNCMe₃)₃(dppm)](PF₆)₂ (a) 3 min, (b) 25 min, and (c) 2 h after sample preparation. Solution c consists almost entirely of the *fac* isomer. Spectrum c was recorded at 0.8 times the gain of spectra a and b.

of the nitrosyl ligand. Of the 12 lines of equal intensity one would expect from this ligand hyperfine interaction, we observe 11, as the center two lines overlap, yielding a single line of relative intensity 2 (Figure 2a). In the methyl isocyanide series *mer*-[Cr(NO)(CNMe)₃(L-L)]²⁺, only a broadening of each component of the ³¹P ligand hyperfine lines was observed, as coupling to ¹⁴N of the nitrosyl ligand was not well resolved. In addition to ligand hyperfine interaction, hyperfine coupling of the spin density with the spin-active chromium nuclei ($I(^{53}\text{Cr}) = 3/2$; 9.54% abundance) leads to a quartet of sidebands (Figure 2), each of which is subject to further splittings by ligand hyperfine effects.

The complexes [Cr(NO)(CNCMe₃)₃(arphos)]^{*n*+} are observed to exist as *mer* isomers, on the basis of their IR spectra; however,

(21) For sweep rates (v) between 50 and 400 mV/s, the ratio $i_p/v^{1/2}$ was constant and $i_{p,a}/i_{p,c} \approx 1$ in accord with diffusion control. The potential separation between anodic and cathodic peaks, ΔE_p , was in the range 90–140 mV for a sweep rate of 200 mV/s. With our cell configuration,²² these properties are consistent with this being a reversible electron-transfer process or a process that approaches reversibility.

(22) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

(23) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

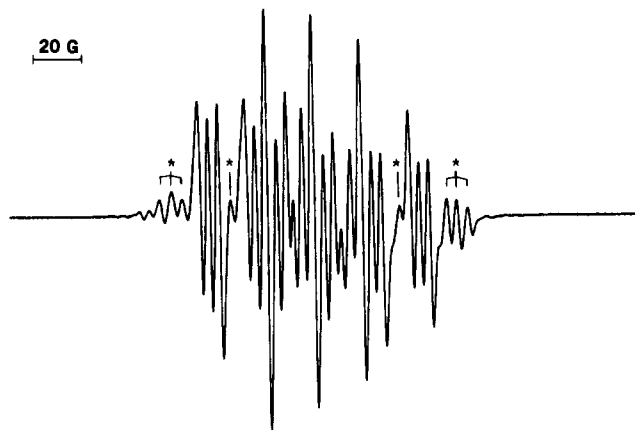
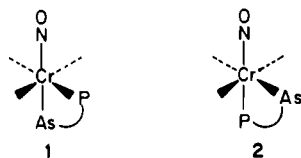


Figure 3. X-Band ESR spectrum of a dichloromethane solution at room temperature containing *mer(cis-P)*-[Cr(NO)(CNCMe₃)₃(arphos)]-(PF₆)₂. Asterisks mark signals that increase in intensity over time due to isomerization to the *fac* isomers.

two different *mer* forms are possible, as allowed by the asymmetry of the chelating ligand. One of the forms contains the phosphorus nucleus *cis* to the nitrosyl ligand (the *mer(cis-P)* isomer, structure 1), while in the other structure the phosphorus is *trans* to the nitrosyl (the *mer(trans-P)* isomer, structure 2). A determination



of the approximate value of $A(^{31}\text{P})$ therefore should allow an unambiguous assignment of the structure. The ESR spectrum of [Cr(NO)(CNCMe₃)₃(arphos)]²⁺ (Figure 3) is complicated by further splitting that arises from the spin-active arsenic nucleus ($I(^{75}\text{As}) = 3/2$; 100% abundance). However, the intensities and spacings between ligand hyperfine lines are consistent only with the phosphorus nucleus being disposed *cis* to the nitrosyl, as $A(^{31}\text{P}) = 30.2$ G. This combination of IR and ESR spectral data allows us to unequivocally assign the structures of [Cr(NO)(CNCMe₃)₃(arphos)]ⁿ⁺ as the *mer(cis-P)* complexes (structure 1).

ESR spectra of the monodentate phosphine derivatives (Table IV) reveal ligand hyperfine interactions with ³¹P and ¹⁴N nuclei, as well as hyperfine coupling to the spin-active ⁵³Cr nuclei. In each case, $A(^{31}\text{P}) \approx 31$ G, consistent with the assignment of these complexes as *cis*-[Cr(NO)(CNCMe₃)₃(PR₃)₂]²⁺. These data, in combination with the IR spectral data of the 1+ compounds, can leave little doubt as to the *cis* configuration of both the 18-electron and 17-electron species in the case of PR₃ = PEtPh₂, PPh₃, and Ph₂Ppy.

Isomerization Studies. The 17-electron complexes *mer*-[Cr(NO)(CNR)₃(L-L)]²⁺ are observed to isomerize slowly in dichloromethane solution, over a period of several hours, to generate the corresponding facial isomer. The ESR spectral data for *fac*-[Cr(NO)(CNR)₃(L-L)]²⁺ are given in Table IV. Isomerizations upon oxidation have now been observed to occur in several cases for the group 6 metals,²⁸ particularly in various derivatives of the carbonyls; examples include the *cis*-*trans* isomerizations of M(CO)₂(P-P)₂ (P-P = Ph₂P(CH₂)_nPPh₂; n = 1, 2, or 3),⁹⁻¹¹ Mo(CO)₄(PR₃)₂,⁸ Mo(CO)₄(carbene)₂,¹² Mo(CO)₂(CNR)₄,¹³ and Mo(CO)₂(CNR)₂(PR₃)₂.¹³ In each of these cases, thermodynamic and kinetic measurements suggest that the isomerizations occur via an intramolecular, nondissociative twist mechanism that proceeds through a trigonal-prismatic intermediate.^{11,13,24} In the *mer*²⁺ → *fac*²⁺ isomerizations of [Cr(NO)(CNR)₃(L-L)]²⁺ this

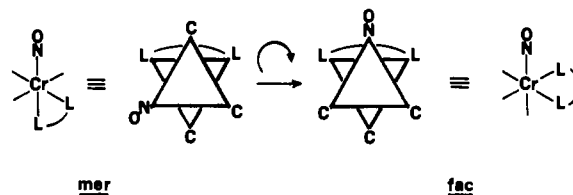


Figure 4. Schematic representation of one trigonal-twist (Bailar) mechanism that could convert *mer*-[Cr(NO)(CNR)₃(L-L)]ⁿ⁺ to its *fac* isomer without bond breaking.

trigonal-twist mechanism, commonly referred to as the “Bailar twist”,²⁵ can easily account for our observations as indicated in Figure 4.

The *mer*²⁺ → *fac*²⁺ isomerization, which can easily be followed by ESR spectroscopy, was observed for all the [Cr(NO)(CNR)₃(L-L)]²⁺ species studied. With the dppm derivative, however, the reaction reached equilibrium faster than that for the other chelate complexes, and the equilibrium mixture consisted almost entirely of the *fac*²⁺ isomer. For example, upon dissolution of a sample of *mer*-[Cr(NO)(CNCMe₃)₃(dppm)](PF₆)₂ in dichloromethane, periodic ESR measurements revealed the isomerization to be essentially complete within 2 h (Figure 2). After this time period, the spectrum did not change over a period of days, although small amounts of the *mer*²⁺ complex were still present (Figure 2c). On the other hand, while the dppe and arphos derivatives also displayed this isomerization behavior, the *mer*²⁺ ⇌ *fac*²⁺ equilibrium was reached only after 1–2 days and the equilibrium mixture consisted of a large proportion of the *mer*²⁺ isomer.²⁶

As one might predict, the strong π-accepting nitrosyl ligand should prefer the weaker π-accepting phosphine ligand in the *trans* position, rather than an RNC ligand (a better π-acid than phosphine). Thus, on simple electronic grounds, we might expect the *mer*-[Cr(NO)(CNR)₃(L-L)]ⁿ⁺ (and *trans*-[Cr(NO)(CNR)₄(PR₃)₂]ⁿ⁺) complexes to be the more stable of the two possible isomers. Any isomerization in these compounds, then,

(25) Bailar, J. C. *J. Inorg. Nucl. Chem.* 1958, 8, 165.

(26) The apparent rate enhancement for the dppm complexes relative to dppe and arphos could result from factors operating within the nondissociative twist mechanism. Thus, in the case of dppm, the single carbon bridge between axial and equatorial phosphorus atoms may be unable to accommodate the strain imposed on the 4-membered M–P–C–P ring, which results from M–P_{ax} bond extension (relative to the shorter M–P_{eq} bond). In the dppe compounds, such ring strain can be alleviated by a simple twisting or puckering of the C₂ bridge²⁷ to yield a 5-membered M–P–C–C–P ring that is relatively strain free. Therefore, in the dppe complexes, isomerization will occur primarily for reasons of steric congestion, whereas in the dppm compounds, additional ring strain could enhance the rate yet still allow isomerization by a nondissociative mechanism. However, an alternative explanation could be that the rate enhancement exhibited by the dppm complexes results from a different mechanism of isomerization, viz. a dissociative process. Some evidence for this mechanism was obtained by examining the isomerization of *mer*-[Cr(NO)(CNCMe₃)₃(dppm)](PF₆)₂ in acetonitrile. The *mer*²⁺ → *fac*²⁺ isomerization occurred at a much slower rate than in the less polar dichloromethane solvent, equilibrium being reached in 6 h vs. 2 h in CH₂Cl₂. The resulting equilibrium mixture was characterized by two ESR-active species, the major one being *fac*-[Cr(NO)(CNCMe₃)₃(dppm)]²⁺ together with a minor component characterized by a *g* value of 1.9959 and ligand hyperfine coupling to only one ³¹P nucleus, situated *cis* to the nitrosyl ligand ($A(^{31}\text{P}) = 31.2$ G and $A(^{14}\text{N}) = 4.5$ G). This species could be formed through the dissociation of the *trans* phosphorus of the dppm ligand, followed by coordination of an acetonitrile molecule, thereby generating six-coordinate [Cr(NO)(CNCMe₃)₃(NCMe)(dppm)]²⁺. Thus, evidence for a monodentate dppm-containing species in acetonitrile, as well as the slower isomerization rate in this solvent as compared to dichloromethane, is consistent with the notion that a dissociative isomerization process could be operative in the case of the dppm derivative.

(27) Dewan, J. C.; Wood, T. E.; Walton, R. A.; Lippard, S. J. *Inorg. Chem.* 1982, 21, 1854.

(28) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes group 3 and 13, etc.

(24) Darensbourg, D. J. *Inorg. Chem.* 1979, 18, 14.

may be construed to occur *primarily* for steric reasons, as a position *cis* to the nitrosyl will be sterically less congested than the *trans* position.

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Supplementary Material Available: Details of the structure solution and full tables of the experimental details (Table S1), atomic parameters (Table S2), anisotropic thermal parameters (Table S3), bond distances and bond angles (Table S4), and observed and calculated structure factors for the crystal structure of $[\text{Cr}(\text{NO})(\text{CNCMe}_3)_3(\text{dppm})]\text{PF}_6$ (60 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del CNR, Florence, Italy

Reactivity of Copper(I) Tetrahydroborates toward CO_2 and COS . Structure of (triphos)Cu($\eta^1\text{-O}_2\text{CH}$)

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The novel tetrahydroborate complexes $(\text{PCy}_3)_2\text{Cu}(\text{BH}_4)$, $(\text{np}_3)\text{Cu}(\text{BH}_4)$ [np_3 = tris(2-(diphenylphosphino)ethyl)amine] and $(\text{etp}_3)\text{Cu}(\text{BH}_4)$ [etp_3 = 1,1,1-tris((diphenylphosphino)ethyl)ethane] have been synthesized and characterized. The reactivity of these compounds and of other copper(I) tetrahydroborates, $(\text{PPh}_3)_2\text{Cu}(\text{BH}_4)$, (triphos)Cu(BH_4) [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane], and $(\text{PMePh}_2)_3\text{Cu}(\text{BH}_4)$, toward CO_2 and COS have been investigated. The latter triatomic molecules are reduced under very mild conditions to give metalloformate or metallothioformate derivatives. The bonding mode of the BH_4^- ligand, i.e. unidentate or bidentate, has been found to influence the rate of the reactions. The reactivity of the formate complex (triphos)Cu(O_2CH) has been investigated in some detail. The latter compound has been studied by X-ray analysis. Crystal data: orthorhombic, space group $Pn2_1a$, a = 20.901 (8) Å, b = 17.136 (6) Å, c = 10.162 (4) Å, Z = 4, R , R_w = 0.055, 0.054 for 2267 reflections having $I \geq 3\sigma(I)$. The bonding mode of the formate group was shown to be through one oxygen atom.

Introduction

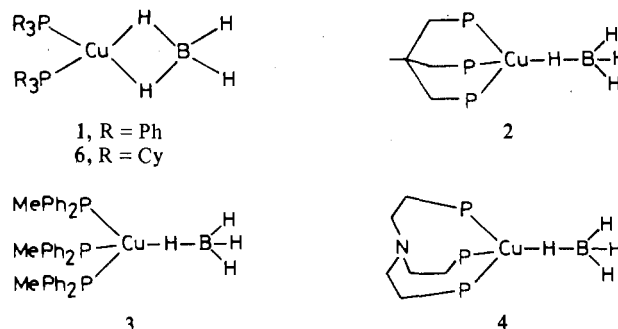
Organic chemists largely use alkali-metal tetrahydroborates to effect the reduction of a plethora of compounds such as ketones or aldehydes to alcohols. At the same time, the tetrahydroborate ion plays an important role in both coordination and organometallic chemistry. Its coordinative properties make the BH_4^- group one of the most versatile ligands, being able to coordinate a metal in a uni-, bi-, or tridentate fashion.¹⁻¹⁰ Bridging BH_4 groups have been also reported.¹¹ The use of tetrahydroborates as sources of hydridic hydrogen atoms is widely exploited by organometallic chemists in a variety of reactions. These include (i) synthesis of hydrido metal complexes,¹² (ii) attack by hydride from BH_4^- on an electrophilic center,¹³ and (iii) reduction of a coordinated species.¹⁴ In addition there is considerable experimental evidence indicative of the action of tetrahydroborates as

effective catalysts for polymerization, oligomerization, and hydrogenation of olefins.¹

In 1978 Sorrell¹⁵ and Fleet¹⁶ reported that the BH_4 moiety in the complex $(\text{PPh}_3)_2\text{Cu}(\eta^2\text{-BH}_4)$ (**1**) is deactivated to the extent that it only reduces carboxylic acid chlorides to aldehydes. This is in contrast to the case of NaBH_4 , which results in further reduction to the alcohol. Since then, the exploitation of **1** as a selective reducing agent in organic chemistry has received increasing attention¹⁷ as attested by the presence of **1** in the recent catalogs of the principal chemical suppliers.¹⁸

Here and in the following paper of this issue we contrast the reactivities of the related heteroallene molecules CO_2 , COS , CS_2 , and SCNPh toward a variety of copper(I) tetrahydroborate complexes with phosphine coligands. These include known compounds such as $(\text{PPh}_3)_2\text{Cu}(\text{BH}_4)$ (**1**),¹⁹ (triphos)Cu(BH_4)⁶ (**2**)

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[triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane], and $(\text{PMePh}_2)_3\text{Cu}(\text{BH}_4)$ (**3**)²⁰ and novel compounds such as $(\text{np}_3)\text{-}$

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