out from the hot solution and unlike the corresponding $P(CH_3)_2C_6H_5$ and $As(CH_3)_2C_6H_5$ reactions, ionic species of the type $RuCl_2(NO)L_3^+$ were not present in the filtrate after removal of the above product.

Triobromo and Triiodo Complexes.—Complexes of the type $RuX_3(NO)L_2$ ($X = Br$ or I; $L = P(CH_3)_2$-C_6H_5, $P(CH_3)(C_6H_5)_2$, $As(CH_3)_2C_6H_5$, or $As(CH_3)$-$(C_6H_5)_2$) may be readily obtained by metathetical replacement of chloride from the corresponding trichloro species or by replacement of chloride and 1 mol of L from the ionic derivatives $[RuCl_2(NO)L_3]B(C_6H_5)_4$ (L $= P(CH_3)_2C_6H_5$ or $As(CH_3)_2C_6H_5$). Such reactions are performed under reflux conditions in ethanol or 2-ethoxyethanol in the presence of a large molar excess of lithium bromide or iodide. The reaction time required for formation of the desired product is *ca.* 6–12 hr, but, with shorter reaction times in several preparations of this type, inseparable mixtures of complexes, presumably of the type $RuCl_xY_{3-x}(NO)L_2$ ($x = 1$ or 2; $Y = Br$ or I), were obtained. This was indicated by the presence of extra resonances at δ values intermediate to those of the trichloro complex and the derived tribromo or triiodo analogs in the ^1H nmr spectrum of dichloromethane solutions of the crude reaction products. In general, longer reaction times were required in the cases where $L = P(CH_3)(C_6H_5)_2$ or $As(CH_3)(C_6H_5)_2$ in order to achieve complete conversion to the required tribromo or triiodo derivatives.

Infrared and Nmr Data.—Unlike the corresponding iridium carbonyl systems,[5] the values of the ruthenium–chloride stretching frequencies in the far-infrared spectra of these complexes do not fall into completely separate groups depending on the ligand in the trans position. However, complexes with configuration I have two bands in the regions 337–322 and 290–284 cm^{-1} which are considered due to vibration of chlorine trans to chlorine and the nitrosyl group, respectively. Complexes with configuration III have four bands in their far-infrared spectra (Table I) in the ruthenium–chloride stretching region. As for the analogous $IrCl_3(CO)[P-(CH_3)_2C_6H_5]_2$, configuration IV, the presence of the extra band is considered due to solid-state splitting, but in the absence of any tribromo or triiodo species of this configuration, unambiguous assignment of these bands is not possible. For the ionic derivatives $[RuCl_2(NO)-L_3]Y$ ($L = P(CH_3)_2C_6H_5$, $Y = Cl$ or $B(C_6H_5)_4$; $L = As(CH_3)_2C_6H_5$, $Y = B(C_6H_5)_4$) the absorptions in the regions 331–328 and 295–280 cm^{-1} are tentatively assigned to ruthenium–chloride stretching, being by far the most intense absorptions in this region. Several ruthenium–bromine stretching frequencies have also been identified in the spectra of the complexes $RuBr_3$-$(NO)L_2$ ($L = P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $As(CH_3)_2$-C_6H_5, or $AsCH_3(C_6H_5)_2$); see Table I.

For the proton nmr data on the complexes listed in Table II the δ values for a particular series of complexes containing the same ligand increase in the order $Cl < Br < I$ which has been interpreted previously[5,6] in terms of increased π bonding in the metal–halogen bond in the order $Cl < Br < I$.

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Substituted Chromium and Molybdenum Carbonyl Complexes of Some Cyanophosphine Ligands[1]

BY CHRISTOPHER E. JONES AND K. J. COSKRAN*

The reactions of the ligands $(C_6H_5)_2PCN$, $C_6H_5P(CN)_2$, $(CH_3)_2PCN$, $(C_2H_5O)_2PCN$, or $[(CH_3)_2N]_2PCN$ with $M(CO)_4C_7H_8$ (M = Cr or Mo and C_7H_8 is norbornadiene) have been investigated. From these reactions, yellow crystalline complexes of the form $[M(CO)_4L]_2$, where L is a bridging cyanophosphine ligand, have been isolated. Their formulation is based on analytical data and their structure is proposed as
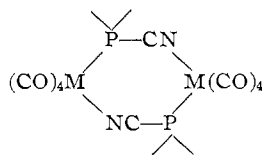
on the basis of the infrared and proton nmr spectral data. These bridged complexes react further with another molar equivalent of ligand L or a different ligand L' to yield complexes of the type $M(CO)_4L_2$ and $M(CO)_4LL'$. The products from these reactions further support the proposed structure for the bridged species. The proton nmr, infrared, and some of the mass spectral data of these bridged complexes are presented and discussed.

Introduction

Cyanophosphine compounds $R_xP(CN)_{3-x}$ ($x = 0$, 1, or 2) have received very little attention as ligands in the area of metal coordination chemistry. In 1963 a disubstituted nickel carbonyl complex of $[(CH_3)_2N]_2$-PCN^2 was reported in which coordination presumably occurred through the phosphorus atom. More recently, Kirk and Smith have reported that $P(CN)_3$

(1) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; see Abstracts, No. INOR-74.

(2) H. Nöth and H. J. Vetter, *Chem. Ber.*, **96**, 1479 (1963).

forms unstable adducts with AlH_3, $AlCl_3$, and $AlBr_3$[3] and in solution an adduct with pyridine[4] was identified by ^{1}H nmr spectroscopy. In the last adduct, $P(CN)_3$ is acting as the acceptor, again with coordination through the phosphorus atom assumed. Finally, some association between the cyanide groups, in both $P(CN)_3$ and $C_6H_5P(CN)_2$, and dimethylformamide[4] was proposed on the basis of ^{1}H nmr data. Because of the relatively little amount of work that has been done in studying the coordination chemistry of cyanophosphine derivatives, this work was begun. Initially, emphasis has been placed on determining the effect of the cyanide group on the coordinating properties of the phosphorus atom to which it is bound and, further, testing whether the cyanide groups are potential donor sites.

The following cyanophosphine ligands were used: $(C_6H_5)_2PCN$, $C_6H_5P(CN)_2$, $(CH_3)_2PCN$, $(C_2H_5O)_2PCN$, and $[(CH_3)_2N]_2PCN$. Metal carbonyls were selected as reactants for these ligands because carbonyl substitution is known to occur for both trivalent phosphorus[5] and nitriles.[5] Also, the resultant complexes are readily amenable to infrared and ^{1}H nmr spectroscopic studies.

While this work was in progress, Nixon and Swain[6] proposed a dimeric structure for the complexes $[M(CO)_4(CF_3)_2PCN]_2$ (M = Cr or Mo) with $(CF_3)_2PCN$ acting as a bridging ligand. It therefore became of interest to determine, by means of chemical and spectroscopic evidence, the nature of dimerization and whether this process could be observed for other cyanophosphine ligands.

Experimental Section

Instrumentation.—The infrared spectra were run on a Perkin-Elmer Model 225 grating spectrophotometer. In all cases $CHCl_3$ was used as a solvent with sodium chloride optics. Proton nmr spectra were taken in $CHCl_3$ and CH_2Cl_2 solutions on a Varian Associates Model A-56/60-D instrument with tetramethylsilane as an internal standard. Elemental analyses and osmometric molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Mass spectra were performed by the Chemical Physics Research Laboratory of the Dow Chemical Co. and were run using the direct probe method with temperatures ranging from 110 to 215°.

Materials.—The ligands were prepared as described elsewhere.[7] Molybdenum norbornadiene tetracarbonyl[8] and chromium norbornadiene tetracarbonyl[8] were also prepared according to previously described methods. All of the preparations were performed under a nitrogen atmosphere with magnetic stirring.

Bridged Complexes.—All of the bridged complexes were prepared by stirring equimolar mixtures of the metal norbornadiene complex and the appropriate ligand in *n*-hexane for several minutes (see Table I). The *n*-hexane was removed on a water aspirator and the remaining solid was recrystallized from dichloromethane to give yellow crystalline solids of the form $[M(CO)_4L]_2$. A molecular weight measurement of $[Mo(CO)_4(C_6H_5)_2PCN]_2$ produced a value of 910; calculated, 838.

Disubstituted Complexes.—The disubstituted complexes (both $M(CO)_4L_2$ and $M(CO)_4LL'$) were prepared by refluxing a 1:1 molar mixture of the appropriate ligand and the bridged metal complex in *n*-hexane from 1 to 4 hr (see Table I). The *n*-hexane was removed on a water aspirator and the remaining solid was recrystallized from *n*-hexane to which a minimum of dichloromethane was added to dissolve the $M(CO)_4L_2$ complexes. The $M(CO)_4LL'$ complexes were recrystallized from *n*-pentane.

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TABLE I
EXPERIMENTAL AND ANALYTICAL DATA

L	Reacn time	—% C— Calcd	Found	—% H— Calcd	Found	—% P— Calcd	Found
		$[Mo(CO)_4L]_2$					
$(C_6H_5)_2PCN$	5 min	48.69	48.68	2.39	2.50	7.40	7.26
$C_6H_5P(CN)_2$[a]	5 min	39.13	36.62	1.36	1.60	8.43	7.81
$(CH_3)_2PCN$	5 min	28.47	28.29	2.03	2.07	10.51	10.39
$(C_2H_5O)_2PCN$	5 min	30.42	30.31	2.82	2.88	8.73	8.59
$[(CH_3)_2N]_2PCN$	5 min	30.59	30.29	3.40	3.45	8.78	8.65
		$[Cr(CO)_4L]_2$					
$(C_6H_5)_2PCN$	5 min	54.50	54.64	2.67	2.75	8.27	8.46
$(CH_3)_2PCN$	5 min	33.47	33.27	2.39	2.40	12.35	12.50
$(C_2H_5O)_2PCN$[a]	12 hr	...	...	...	...	...	...
$[(CH_3)_2N]_2PCN$	12 hr	34.95	34.70	3.88	3.84	10.03	10.22
		$Mo(CO)_4L_2$					
$(C_6H_5)_2PCN$	2 hr	57.14	57.12	3.17	3.23	9.84	9.65
$(CH_3)_2PCN$	1 hr	31.41	31.18	3.14	3.22	16.23	15.92
$(C_2H_5O)_2PCN$[a]	2 hr	...	...	...	...	...	...
$[(CH_3)_2N]_2PCN$[a]	1 hr	33.73	31.18	4.82	4.84	12.45	11.31
		$Cr(CO)_4L_2$					
$(C_6H_5)_2PCN$	4 hr	61.43	59.81	3.41	3.89	10.58	10.28
$(CH_3)_2PCN$[a]	2 hr	...	...	...	...	...	...
$[(CH_3)_2N]_2PCN$[a]	2 hr	36.99	35.97	5.28	5.69	13.64	10.28
		$Mo(CO)_4LL'$					
$[(CH_3)_2N]_2PCN$ (L) $(CH_3O)_3P$ (L')	1 hr	30.19	30.30	4.40	4.52	13.00	12.88
		$Cr(CO)_4LL'$					
$[(CH_3)_2N]_2PCN$ (L) $(CH_3O)_3P$ (L')	1 hr	33.26	32.72	4.85	4.77	14.32	14.25

[a] Readily decomposed and, therefore, not isolated in purity suitable for good analysis; however, infrared and nmr spectra gave unequivocal evidence as to the identity of these complexes.

Results and Discussion

The bridged complexes were readily prepared in almost quantitative yields when molybdenum norbornadiene tetracarbonyl was allowed to react with 1 molar equiv of the ligands. The chromium analogs, however, were prepared with slightly more difficulty and in lower yields. For both metals the formation of the bridged complexes was indicated by the appearance of a bright yellow precipitate. A facile reaction was observed for diphenyl- and dimethylcyanophosphines for both metals, while the diethyl cyanophosphite and bis-(dimethylamino)cyanophosphine ligands, although readily reacting with molybdenum, reacted substantially slower with chromium (Table I) and gave poor yields of the bridged complex. In addition, these latter complexes were not nearly as stable to decomposition as the others. The chromium complexes of all four ligands and the molybdenum complex of diethyl cyanophosphite slowly decomposed upon exposure to air. The other molybdenum complexes were somewhat more stable.

When 2 mol of ligand was added to the metal norbornadiene tetracarbonyl complex, the bridged complex would again precipitate from solution. However, if this solution was then refluxed for about 1 hr, the bridged species gradually went into solution as the monomeric disubstituted complex $M(CO)_4L_2$ formed. In a similar manner, the bridged species could undergo a reaction with a second mole of a different phosphorus ligand (L') to give $M(CO)_4LL'$. The ease with which these reactions took place paralleled that for the bridged complexes. These disubstituted monomeric species were found to be unstable to air possibly because of the hygroscopic nature of the cyanide group. This can be compared to $P(CN)_3$ which is reported to be extremely

TABLE II
SPECTRAL DATA[a]

Compounds	Infrared ν(C≡N)[c]	Infrared ν(C≡O)[d]	¹H nmr[b] δ[e]	¹H nmr[b] J_{P-H}
(C₆H₅)₂PCN	2173		7.20 m	9.0[f]
C₆H₅P(CN)₂	2184, 2092		7.60 m	10.0[f]
(CH₃)₂PCN	2172		1.47 d	4.5
(C₂H₆O)₂PCN	2180		1.30 m (CH₃)	...
			4.08 m (CH₂)	7.5
[(CH₃)₂N]₂PCN	2168		2.75 d	10.0
[Mo(CO)₄L]₂				
L = (C₆H₅)₂PCN	2161	2031, 1945, 1886	7.55 m	...
L = C₆H₅P(CN)₂	2170, 2155	2044, 1965, 1920	...	...[g]
L = (CH₃)₂PCN	2163	2028, 1935, 1887	1.94 d	6.0
L = (C₂H₆O)₂PCN	2164	2037, 1946, 1906	1.30 m (CH₃)	...
			3.70 m (CH₂)	7.0
L = [(CH₃)₂N]₂PCN	2159	2025, 1932, 1881	2.82 d	11.6
[Cr(CO)₄L]₂				
L = (C₆H₅)₂PCN	2158	2023, 1930, 1885	7.50 m	...
L = (CH₃)₂PCN	2161	2020, 1934, 1885	1.92 d	5.0
L = (C₂H₆O)₂PCN	2150	2025, 1985, 1930	1.41 m (CH₃)	...
			4.20 m (CH₂)	7.0
L = [(CH₃)₂N]₂PCN	2155	2018, 1927, 1886	2.79 d	11.0
Mo(CO)₄L₂				
L = (C₆H₅)₂PCN	2183	2039, 1955, 1932	7.40 m	...
L = (CH₃)₂PCN	2183	2040, 1950, 1925	1.95 "t"	5.7
L = (C₂H₆O)₂PCN	2183	2062, 1997, 1970	1.45 m (CH₃)	...
			4.20 m (CH₂)	7.0
L = [(CH₃)₂N]₂PCN	2176	2037, 1945, 1924	2.82 "t"	11.6
Cr(CO)₄L₂				
L = (C₆H₅)₂PCN (trans)	2182	1925	7.40 m	...
L = (CH₃)₂PCN	2182	2031, 1945, 1918	1.93 "t"	6.8
L = [(CH₃)₂N]₂PCN (trans)	2173	1917	2.76 "t"	11.8
Mo(CO)₄LL'				
L = [(CH₃)₂N]₂PCN	2175	2035, 1960, 1920	2.71 "t"	11.8
L' = (CH₃O)₃P			3.55 "t"	11.2
L = [(CH₃)₂N]₂PCN	2175	2040, 1965, 1930	2.75 "t"	11.6
L' = P(OCH₂)₃CCH₃			4.19 "t" (CH₂)	4.1
Cr(CO)₄LL' (trans)				
L = [(CH₃)₂N]₂PCN	2185	1918	2.74 "t"	11.6
L' = (CH₃O)₃P			3.64 "t"	11.2

[a] All spectra of complexes taken in CHCl₃, except nmr spectra of phenyl derivatives which were obtained in CH₂Cl₂. [b] Chemical shifts are in ppm (±0.05) and are referenced to tetramethylsilane. Coupling constants are in Hz (±0.5). [c] CN stretches in complexes were all medium to very weak in intensity. [d] Disubstituted monomeric complexes were of cis configuration unless otherwise indicated. [e] Abbreviations: m, multiplet; d, doublet; "t," apparent triplet due to virtual coupling. [f] Coupling to ortho protons. [g] Not sufficiently soluble for nmr spectrum.

sensitive to moisture yet inert to oxygen at room temperature.[9]

Infrared Data.—Table II lists the infrared data for the carbonyl and cyanide stretching regions for all of the complexes characterized in this work. Figure 1 shows the shapes and intensities of the bands in the CO
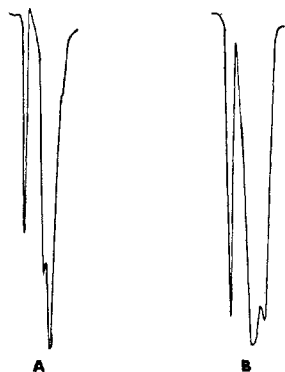

Figure 1.—Shapes of the infrared bands in the CO region. A represents the general shape of the cis-disubstituted complexes and B that of the bridged complexes.

region of both the disubstituted complexes and the bridged complexes. All of the disubstituted complexes of molybdenum are white and cis disubstituted while the chromium analogs are yellow and trans disubstituted with the exception of the complex of (CH₃)₂PCN which is cis. The C_{2v} (cis) and D_{4h} (trans) symmetries of these complexes are readily indicated by the number and intensity of the carbonyl stretching frequencies[10] (Table II, Figure 1). The trans-disubstituted complexes of chromium may indicate that a sterically hindered arrangement exists in the cis isomers with the bulkier ligands and that a cis–trans rearrangement takes place after initial attack of the bridged complex by a ligand (see later). This steric factor is apparently not significant for the larger molybdenum atom and the cis configuration results. For the bridged complexes the CO stretching vibrations probably conform to a local C_{2v} carbonyl environment requiring four CO stretching frequencies (2 A₁ + B₁ + B₂). In general, the more intense B₂ band is of lower energy than the B₁ band for the cis-disubstituted complexes. In the bridged case, however, it appears that the reverse may be true, with the B₁ band being a low-energy shoulder on the B₂ band. Regardless of the assignment of these

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bands, however, the shapes of the absorptions (Figure 1) were indicative of the complex present.

The cyanide stretching mode was useful in identifying the resulting complexes, although not nearly as useful as the carbonyl band. The CN stretching frequency for the bridging ligands occurs at lower energy than that of the free ligand (Table II). These shifts to lower energy ranged from 9 to 30 cm^{-1} with the largest shift occurring with the Cr complex of $(C_2H_5O)_2PCN$. It may be significant that the largest shift occurs with the ligand with the most electronegative group attached to phosphorus since Nixon and Swain[6] observed a similar shift of 40 cm^{-1} for the Cr and Mo complexes of $(CF_3)_2PCN$. It is interesting to note that this shift to lower energy for the CN stretch in these bridging cyanophosphines is opposite to the shift observed for a bridging thiocyanate ion,[11] which has a higher energy CN stretching frequency than a terminal thiocyanate group. Furthermore, the CN stretching frequency for nitrile (RCN) complexes[12,13] similarly shows an increase over that of the uncomplexed nitrile. Gerrard, *et al.*,[14] and Stolz, *et al.*,[15] have discussed the increase in ν_{CN} for nitriles upon coordination in terms of mesomeric forms for the nitrile; which are not possible in the complexed nitrile. In the R_2PCN-bridged complexes the lower ν_{CN} value over that of the free ligand value may be the result of the structure restrictions of the bridged complex. If the nitrogen atom is sp hybridized ($-C\equiv N:$), then a near-linear arrangement of the atoms P–C–N–M must result (M = Cr or Mo). This linear arrangement would place a strain on the M–P–C angles. However, if the sp hybrid orbital on nitrogen has some p character, which in the limit would be sp^2 hybridized ($-C=\ddot{N}:$), then a smaller C–N–M angle would result which would be more compatible with the bridged structure by relieving ring strain. The carbon–nitrogen bond would in turn be slightly weakened and a lowering of the CN stretching frequency would be observed.

For the disubstituted complexes of these phosphorus cyanide ligands, the CN stretching frequency for the now terminal CN group either remains essentially the same as the free ligand or actually increases slightly in energy. The cyanide stretching region for the bridged molybdenum complex with the ligand $C_6H_5P(CN)_2$ exhibits two different cyanide stretching frequencies, one bridging and one free, indicating that, despite the two available nitrogen bonding sites, the same method of bridging as observed for R_2PCN is employed, thus retaining the eight-membered ring.

Proton Nmr.—The proton nmr spectra for the ligands have been described elsewhere[7] and are shown in Table II for comparison. The spectra of the bridged complexes are not significantly different from those of the free ligands except for a downfield shift in the resonances. The spectra of the disubstituted species conformed to an $X_nAA'X'_n$ type of spectrum,[16,17] where X and A are the

protons and phosphorus of one ligand and X' and A' are the protons and phosphorus of a second identical ligand cis or trans to the first. When the organic group attached to the phosphorus was either $-C_6H_5$ or $-OC_2H_5$, the spectra were further complicated by the added proton–proton coupling. However, in the case of $(CH_3)_2PCN$ or $[(CH_3)_2N]_2PCN$ a simpler spectrum was obtained which was useful in structural determinations (see below). For the disubstituted complexes [M-$(CO)_4L_2$] of these latter two ligands the $X_nAA'X'_n$ spectra were each observed to consist of a doublet of separation $|J_{AX} + J_{AX'}|$[17] plus a central peak of varying intensity. The magnitude of this central resonance has been related to the magnitude of $J_{PP'}$.[16,17] The disubstituted molybdenum and chromium complexes which were cis and trans, respectively (with the exception of cis-$Cr(CO)_4[(CH_3)_2PCN]_2$), exhibited very weak central peaks and small ^{31}P–^{31}P coupling, consistent with other disubstituted complexes of this geometry.[16,18–21] It has been observed previously that cis-disubstituted chromium complexes have very strong phosphorus–phosphorus coupling[19,21–23] (stronger than trans-disubstituted chromium). This is demonstrated here by an intense central peak for the complex cis-$Cr(CO)_4$-$[(CH_3)_2PCN]_2$.

The proton nmr spectra of the mixed-ligand complexes can be considered an M_mABY_n spin system similar to that discussed by Ogilvie, *et al.*,[23] where A and B are the phosphorus atoms and M and Y are the protons. Accordingly, if $J_{AB} \ll \nu_A - \nu_B$, then a doublet is observed for each set of protons split by the adjacent phosphorus atom. If $J_{AB} \approx \nu_A - \nu_B$, then perturbation of the doublet spectrum occurs (see Figure 2), and if $J_{AB} \gg \nu_A - \nu_B$, apparent "triplets" due to virtual coupling are observed (see Figure 2). Of the three mixed-ligand complexes reported in Table II only the Mo compound, where L = $[(CH_3)_2N]_2PCN$ and L' = $(CH_3O)_3P$, exhibited apparent "triplets" in the ^1H nmr spectrum with very weak central peaks (Figure 2). In a previous study[23] of mixed-ligand complexes, only examples of the first two cases outlined above, $J_{AB} \ll \nu_A - \nu_B$ and $J_{AB} \approx \nu_A - \nu_B$, had been observed. The spectrum of the lone Cr mixed-ligand complex is best described as that of a perturbed doublet[23] (Figure 2), while the spectrum of the remaining Mo complex with L = $[(CH_3)_2N]_2PCN$ and L' = $P(OCH_2)_3CCH_3$ is essentially just two doublets; an example of the case where $J_{AB} \ll \nu_A - \nu_B$.

Mass Spectra.—Nixon and Swain reported[6] for their dimeric complexes of $(CF_3)_2PCN$ that they observed mass spectra characterized by fragmentation patterns showing stepwise loss of all eight carbonyl groups while the $(MPCN)_2$ ring system remained intact. Of the complexes reported in this work, mass spectra have been obtained for $[Mo(CO)_4L]_2$ where L = $(C_6H_5)_2$-PCN, $C_6H_5P(CN)_2$, $(CH_3)_2PCN$, and $[(CH_3)_2N]_2PCN$ and for $\{Cr(CO)_4[(CH_3)_2N]_2PCN\}_2$. In these cases,

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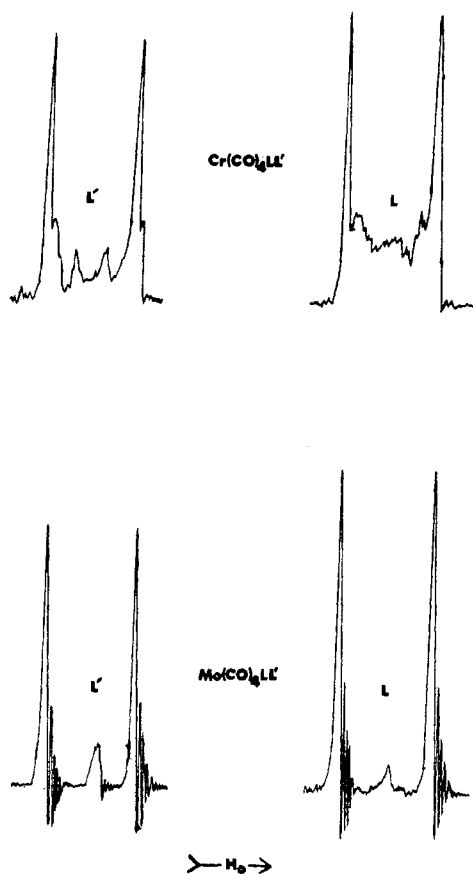
Figure 2.—Hydrogen-1 nmr spectra of the mixed-ligand complexes. In both the Cr and the Mo complexes, L = [(CH₃)₂N]₂PCN and L' = (CH₃O)₃P. (See Table II for chemical shifts and and coupling constants.)

only the complexes with L = [(CH₃)₂N]PCN showed parent ions and indicated fragmentation patterns similar to those reported by Nixon and Swain.[6] For the (C₆H₅)₂PCN and (CH₃)₂PCN complexes, the predominant fragmentation patterns originated from the recombination ions of (CO)₅MoL⁺ and Mo(CO)₆⁺. In these cases there may very well be rapid cleavage of the dimer, as a result of the metal–nitrogen bonds breaking, leaving a species of the form M(CO)₄L⁺, followed by combination with CO. The only exception to this was the C₆H₅P(CN)₂ complex where only rapid decomposition of the entire complex was observed.

Structure.—The identity of the yellow crystalline solids obtained by the displacement of norbornadiene from C₇H₈M(CO)₄ with these cyanophosphine ligands was established by elemental analysis as being [M-(CO)₄L]ₙ, and the value of 2 for *n*, which was expected because of the two potential bonding sights on each ligand, was confirmed by molecular weight measurements in one case (see Experimental Section) and the observation of some parent ions in the mass spectra.

Therefore, as suggested by Nixon and Swain for the complexes of (CF₃)₂PCN,[6] the dimeric structure involving two bridging cyanophosphine ligands is proposed.

There are two possible isomers for this type of dimer (excluding CO bridging) (see Figure 3): one in which a

Figure 3.—Two possible isomers for the bridged dimeric complex. Dotted lines indicate expected cleavage by a phosphorus ligand.

given metal atom is bound to the phosphorus atom of one ligand and the nitrogen atom of the other (A) and a less symmetric isomer with both phosphorus atoms bound to the same metal (B). The products obtained from the reactions of these bridged complexes with other ligands as well as the proton nmr and infrared spectra all indicate that the more symmetric of the two isomers (A) is the only isomer present

When a dimeric complex bridged with ligand L is treated with L', it is expected that the metal–nitrogen bond is cleaved to yield 2 mol of a disubstituted product. If one assumes that, for the dimer, the less symmetric structure (B) is present, then the complex would be expected to cleave asymmetrically to yield two distinct complexes, M(CO)₄L₂ and M(CO)₄L'₂. However, if the more symmetric structure (A) is present, symmetric cleavage of the complex to yield 2 mol of M(CO)₄LL' would be expected. Since the mixed-ligand complex is exclusively produced in these reactions, and if there is no rearrangement occurring, isomer B can be ruled out. Additional support for isomer A comes from the proton nmr and infrared spectra. The more symmetric isomer (A) has only one carbonyl environment, while structure B would have two distinct environments. In the infrared spectra only one type of carbonyl group is observed. The nmr spectra of the cis-disubstituted complexes M(CO)₄L₂, where L = (CH₃)₂PCN or [(CH₃)₂N]₂PCN, clearly show the presence of virtual coupling. If, in the bridged complex, isomer B were present, with two phosphorus atoms bound in a cis configuration to a single metal atom, one would expect to see more indication of virtual coupling in the nmr spectra. The spectra are sharp doublets with no evidence of virtual coupling, further indicating the presence of the more symmetric isomer (A).