the empty $d_{x^2-y^2}$ orbital on phosphorus offering the possibility of bonding similar to that of the metal sandwich complexes. Such a π interaction is consistent with the single downfield ring proton resonance indicative of equivalent environments of the ring hydrogen atoms and may explain the facile nature of the exchange evidenced by our NMR results.

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Phosphorus-31 Nuclear Magnetic Resonance Spectra of *fac* and *mer* Isomers of Tricarbonylbis[bis-(diphenylphosphino)methane]molybdenum

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The distinction between *fac* and *mer* isomers of L₃Mo(CO)₃ compounds is often made on the basis of infrared spectroscopy.[1-4] For certain ligands, notably phenyldimethylphosphine, proton NMR spectroscopy may distinguish the isomers, although not always conclusively.[4] In other phosphine ligands lacking such convenient alkyl groups (e.g., triphenylphosphine), proton NMR spectroscopy is of little stereochemical value. Such is the case with the ligand bis(diphenylphosphino)-methane (dpm), for which we report here the *fac* and *mer* complexes (OC)₃Mo(dpm)₂. We show that ³¹P NMR spectroscopy makes possible an unequivocal assignment of the isomers in this and presumably in other cases. Furthermore, the results are of interest in relation to recent studies of the ³¹P spectra of chelating phosphines.

Experimental Section

Reagents. Bis(diphenylphosphino)methane purchased from Strem Chemicals Inc. was used without further purification. Preparation of $(1-6-\eta-C_7H_8)Mo(CO)_3$ followed a reported method.[5]

Physical Measurements. Infrared spectra of the carbonyl region were measured on a Perkin-Elmer Model 337 spectrometer equipped with an external recorder and were calibrated with bands of CO and DBr. The proton-decoupled ³¹P NMR spectra were obtained on a Bruker HFX-90 operating at 36.4 MHz using a deuterium lock and a sealed capillary of P₄O₆ as an external standard. The chemical shift values are quoted relative to 85% H₃PO₄ which was taken to be 112.5 ppm upfield from P₄O₆. Microanalyses were performed by the Microanalytical Laboratory of this department.

Preparation of *fac*-(CO)₃Mo(Ph₂PCH₂PPh₂)₂. Bis(diphenyl-phosphino)methane (2.2 g, 5.7 mmol) and $(1-6-\eta-C_7H_8)Mo(CO)_3$ (0.5 g, 1.8 mmol) were dissolved in 50 ml of dichloromethane at room temperature. The solution turned pale yellow almost immediately and was stirred for 1 hr. After filtration, diethyl ether (50 ml) was added and the solution was chilled overnight at 0° to precipitate off-white crystals. These were recrystallized from dichloro-
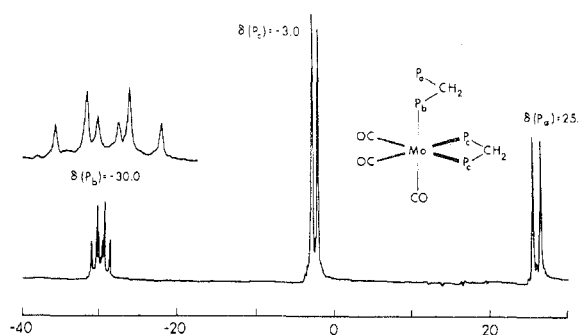
Figure 1. ³¹P NMR spectrum of *fac*-(OC)₃Mo(dpm)₂ in CD₂Cl₂; chemical shifts in ppm relative to 85% H₃PO₄, with negative values downfield from reference. Coupling constants are $|^2J_{ab}|$ = 34.2 Hz, $|^2J_{bc}|$ = 24.4 Hz.

methane–ether affording the analytical sample (yield 1.5 g, 86%, mp 178–180°). Anal. Calcd for C₅₅H₄₄O₃P₄Mo: C, 67.10; H, 4.67. Found: C, 66.88; H, 4.45. Infrared spectrum (ν_{CO} in cm⁻¹, relative intensities in parentheses): CH₂Cl₂, 1943 (10.0), 1848 (9.6, br); Nujol mull, 1938 (10.0), 1840 (10.0), 1825 (10.0).

Preparation of *mer*-(CO)₃Mo(Ph₂PCH₂PPh₂)₂. Bis(diphenyl-phosphino)methane (2.2 g, 5.7 mmol) and $(1-6-\eta-C_7H_8)Mo(CO)_3$ (0.5 g, 5.7 mmol) were stirred in benzene (30 ml) for 15 min. Solvent was removed from the yellow solution under reduced pressure, and the residue was recrystallized from dichloromethane–ether affording yellow crystals of the *mer* isomer (yield 1.6 g, 91%, mp 184–186°). Anal. Calcd for C₅₅H₄₄O₃P₄Mo: C, 67.10; H, 4.67. Found: C, 66.70; H, 4.70. Infrared spectrum (ν_{CO} in cm⁻¹, relative intensities in parentheses): CH₂Cl₂, 1969 (2.2), 1867 (10.0), 1841 (6.0, sh); Nujol mull, 1959 (6.0), 1858 (8.1, sh), 1845 (10.0).

Results and Discussion

The displacement of cycloheptatriene from $(1-6-\eta-C_7H_8)Mo(CO)_3$ by phosphines leads normally to the facial isomer of (OC)₃MoL₃.[6] Using dpm in dichloromethane at room temperature, we have obtained the anticipated *fac*-(OC)₃Mo(dpm)₂. However, the same reaction peformed at room temperature in benzene leads exclusively to the meridional form. Since isomerization of *fac* to *mer* is slow even in refluxing benzene, we conclude that the *fac* complex is not an intermeidate in the formation of the *mer* form in this solvent. This pronounced solvent effect is the more remarkable in view of the reported reaction of bis(diphenylstibino)methane with the cycloheptatriene complex in benzene to form *fac*-(OC)₃Mo(Ph₂SbCH₂SbPh₂)₂.[7]

The *fac* isomer is expected to show two carbonyl stretching bands (both strong) and the *mer* three (one strong) and the assignments made on this basis are in accord with those from ³¹P NMR spectra (see below).

The ³¹P NMR spectrum of *fac*-(OC)₃Mo(dpm)₂ is shown in Figure 1 and indicates three types of phosphorus atoms in the ratio 1:2:1. The doublet of triplets at lowest field is assigned to Pb, the coordinated phosphorus of the monodentate dpm; it is split into a doublet by the uncomplexed Pa which is further split into triplets by the two chemically equivalent atoms, Pc, of the chelate. The high-field doublet, which has a chemical shift very similar to that of free dpm, is assigned to the uncoordinated phosphorus atom Pa. The doublet at lower field corresponds to the chelating phosphorus atoms Pc.

The ³¹P NMR spectrum of the *mer* isomer (Figure 2) shows four signals, since the phosphorus atoms of the chelate are no longer equivalent. The doublet at highest field is again assigned to the uncomplexed Pa while the doublet of quartets at lowest field must be assigned to Pb. The apparent triplet resonance is assigned to Pc which would be expected to have similar coupling constants to Pb and Pd since it is cis to both. The remaining resonance is a doublet of doublets as expected for Pd. The chemical shifts observed for the phosphorus atoms of chelated dpm are shielded by approximately 30 ppm as

Notes
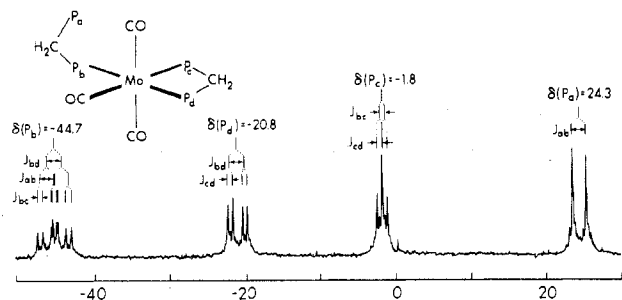
Figure 2. ^{31}P NMR spectrum of *mer*-(OC)$_3$Mo(dpm)$_2$ in CD$_2$Cl$_2$, chemical shifts in ppm relative to 85% H$_3$PO$_4$, with negative values downfield from reference. Coupling constants are $|^2J_{ab}|$ = 64.4 Hz, $|^2J_{bc}|$ = 25.6 Hz, $|^2J_{bd}|$ = 72.4 Hz, $|^2J_{cd}|$ = 24.4 Hz.

compared to the coordinated phosphorus atom of monodentate dpm. We have observed the same trend in other dpm complexes of molybdenum and iron.[8] In contrast, it is well established that chemical shifts of phosphorus atoms in five-membered chelate rings show a large downfield shift relative to unchelated coordinated phosphorus.[9,10]

Registry No. *fac*-(OC)$_3$Mo(dpm)$_2$, 56009-06-4; *mer*-(OC)$_3$Mo(dpm)$_2$, 56085-32-6; (1-6-η-C$_7$H$_8$)Mo(CO)$_3$, 12125-77-8; ^{31}P, 7723-14-0.

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The Interaction of HCN with [Ru(NH3)5H2O]2+

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The rearrangement of N-bound imidazole to the C-bound form when it is ligated to Ru(II) and the labilization of the trans position by the C-bound form[1] prompted the present study which is concerned with the formation of the HCN complex of Ru(II), and with the subsequent reactions of the species. Some observations on the complex when it is formed as product of the decomposition of [Ru(NH3)5NCBH3]$^+$ have been reported by Ford.[2] These observations have been amplified and modified by this work in which the instability of the ion [Ru(NH3)5HCN]$^{2+}$ is attributed to intramolecular rearrangement of the N-bound to the C-bound, resulting in labilization of the trans ammonia and subsequent polymerization.

Experimental Results and Discussion

A solid of composition Ru(NH3)5(HCN)(PF6)2 (I) was prepared by the following procedure. Oxygen-free HCN was bubbled through [Ru(NH3)5(H2O)]$^{2+}$ in 6 *M* trifluoroacetic
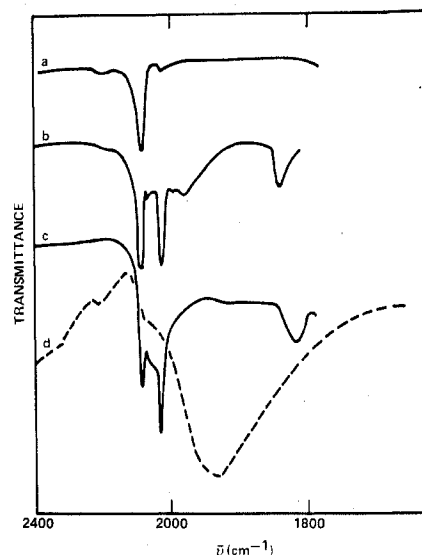
Figure 1. Infrared spectra in the region 2000–1800 cm^{-1} for the rearrangement of [Ru(NH$_3$)$_5$NCH](PF$_6$)$_2$ (KBr pellets): (1a) freshly prepared (6 *M* acid); (1b and 1c) 1 and 0.1 *M* acid, respectively; (1d) after addition of NH$_3$ to I and reprecipitation. Similar spectra were obtained when I was aged for periods of days.

Table I. Infrared Frequencies (ν(C$\equiv$N)) for Free and Coordinated Nitriles

Compd	ν(CN), cm^{-1}	Ref
CH$_3$CN	2254	2
HCN	2097	2
NaCN	2080	3
[Ru(NH$_3$)$_5$NCCH$_3$](BF$_4$)$_2$	2239	2
[Ru(NH$_3$)$_5$NCH](ClO$_4$)$_2$	1960 vs, b	2
[Ru(NH$_3$)$_5$NCH](PF$_6$)$_2$	2085	This work
[Ru(NH$_3$)$_5$CN]PF$_6$	1998	This work

acid for 15 min, resulting in a pale yellow solution. On addition of excess NH4PF6 a light yellow solid was precipitated in high yield, ca. 70%. Elemental analysis of the solid was consistent with the formulation [Ru(NH3)5(NCH)](PF6)2. Calcd: C, 2.39; H, 3.20; N, 16.69. Found: C, 2.50; H, 3.17; N, 16.16.

The infrared spectra recorded for the salt [Ru(NH3)5N-CH](PF6)2 are shown in Figure 1. Different nitrile stretching frequencies were found depending on the conditions used for the preparation. When I is freshly prepared (the freshly prepared material only will hereinafter be designated as I) under strict exclusion of oxygen in strongly acidic conditions (ca. 6 *M* acid), the spectrum shown in Figure 1a is obtained (ν(CN) 2080 cm^{-1}). Figures 1b and 1c show the spectra obtained when the preparation was carried out under less acidic conditions (less then 1 *M* acid). Aging of I resulted in a progression of absorption bands similar to those shown in Figures 1b, 1c, and 1d. When a solution of [Ru(NH3)5-(H2O)]$^{2+}$ is treated with an equimolar solution of sodium cyanide, the solid, precipitated as a PF6$^-$ salt, shows one strong, sharp band, ν(CN) 1998 cm^{-1}. Table I summarizes the infrared frequencies (ν(CN)) for free and coordinated nitriles, including results reported by Ford.[2]

The behavior described taken together with consideration of the conditions for the preparation of I imply that the compound is the N-bound HCN complex, analogous to the acetonitrile complex of Ru(II). This supposition is supported by the fact that I shows a band maximum at 238 nm (log ϵ ~4) which can be compared with the band maximum for [Ru(NH3)5NCCH3]$^{2+}$ at 229 nm (log ϵ 4.2).[3]

The immediate product of the reaction of Ru-(NH3)5NCBH3$^+$ with 2 *M* HCl is reported[2] to have an absorption band with a maximum at 241 nm and with ϵ ~4, in good agreement with our measurements for the ion we