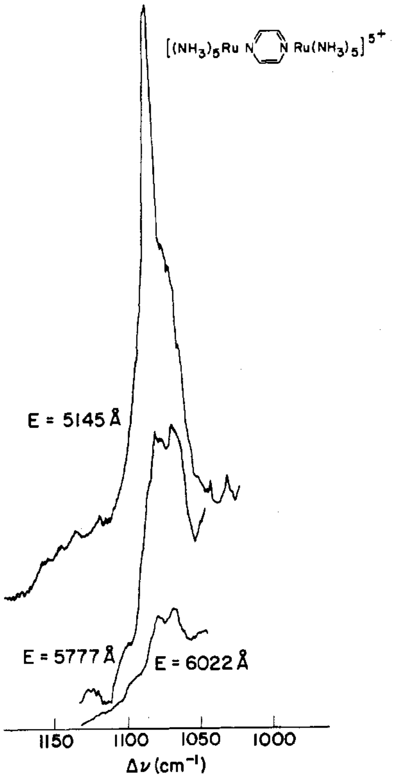

Figure 2. The 1080- and 1070-cm^{-1} features of the Raman spectrum of $[(NH_3)_5Ru\text{-}pyr\text{-}Ru(NH_3)_5]^{5+}$, obtained with a spinning cell, at various excitation wavelengths, *E*.

(II,II) spectrum. With excitation in the middle of the absorption band, this Raman feature appears as a shoulder on the intense 1080-cm^{-1} (ν_1) band. As the excitation is moved to the low-energy side of the absorption band, the 1080-cm^{-1} band loses intensity rapidly, while the 1070-cm^{-1} band intensity change is much less. The effect is shown in Figure 2; with 6022-Å excitation the 1070-cm^{-1} band is actually stronger than the 1080-cm^{-1} band. Clearly the 1080-cm^{-1} band is enhanced via the Ru(II) → pyr charge-transfer transition, but the 1070-cm^{-1} band is not. Therefore, the 1070-cm^{-1} band is assignable to the ν_1 component arising from the Ru(III) end of the complex.

The Fermi resonance observed for this fundamental in (III,III) is not seen in the (II,III) spectrum although the weakness of the 1070-cm^{-1} band makes it difficult to preclude another, still weaker, component. It is plausible, however, that the increase of the ν_1 frequency to 1070 cm^{-1} from ~1044 cm^{-1} in (III,III) significantly weakens the Fermi interaction. Other components assignable to the Ru(III) center should also appear in the off-resonance (II,III) spectrum, but the great disparity between resonance-enhanced and non-resonance-enhanced bands has so far precluded their observation.

Table I summarizes our assignments of the observed Raman features, on the assumption that the trapped-valence formulation of (II,III) is valid. Direct evidence for this formulation consists of the one band, 1070 cm^{-1}, attributable to Ru(III), and the resonance enhancement and close frequency correspondence to (II,II) of the bands assignable to Ru(II).

Registry No. $[(NH_3)_5Ru\text{-}pyr\text{-}Ru(NH_3)_5]^{4+}$, 26253-76-9; $[(NH_3)_5Ru\text{-}pyr\text{-}Ru(NH_3)_5]^{5+}$, 35599-57-6; $[(NH_3)_5Ru\text{-}pyr\text{-}Ru(NH_3)_5]^{6+}$, 38900-60-6.

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Protonation of the Metal–Metal Bond in $[\mu\text{-}(SCH_3)Fe(CO)_2L]_2$ Complexes (L = $P(CH_3)_{3-x}(C_6H_5)_x$). Experimental Evidence of the Variation of Nucleophilicity of the Metal–Metal Bond with Donor Properties of Phosphorus Ligands

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A recent publication on the protonation of the metal–metal bond in dinuclear complexes[1] prompts us to report our observations on the protonation of $[\mu\text{-}(SCH_3)Fe(CO)_2L]_2$ compounds. Although these compounds have been known for a long time,[2] a reexamination of the behavior of $[\mu\text{-}(SCH_3)Fe(CO)_3]_2$ toward phosphines has only recently appeared.[3] Furthermore, except for the action of halogens on $[\mu\text{-}(SR)Fe(CO)_2L]_2$,[4] no study has been made of the reactivity of these compounds containing a metal–metal bond toward electrophilic reagents.

We have therefore investigated the behavior of $[\mu\text{-}(SCH_3)Fe(CO)_2L]_2$ complexes toward a proton. An important difference having appeared in the behavior of complexes when L = $P(CH_3)_3$ or $P(C_6H_5)_3$, we have, for this reason, extended the study of the reactivity toward a proton to the series with L = $P(CH_3)_{3-x}(C_6H_5)_x$ (x = 0–3). For these complexes the proposed structure is that in which the ligands L are trans to the metal–metal bond and the SCH_3 have the syn-endo position.[3]

Experimental Section

All of the reactions have been done under a nitrogen atmosphere. The ligands $P(CH_3)_3$,[5] $P(CH_3)_2(C_6H_5)$,[6] and $P(CH_3)(C_6H_5)_2$[6] have been prepared following literature methods. $P(C_6H_5)_3$ and $[\mu\text{-}(SCH_3)Fe(CO)_3]_2$ are of commercial origin and have been used without further purification.

The syntheses of $[\mu\text{-}(SCH_3)Fe(CO)_2L]_2$ compounds have been performed according to published procedures[3] with slight modifications. Infrared spectra were recorded on a Perkin-Elmer 225 and NMR spectra were obtained with a Varian A-60A.

Protonation of $[\mu\text{-}(SCH_3)Fe(CO)_2P(CH_3)_3]_2$ (I) and $[\mu\text{-}(SCH_3)Fe(CO)_2P(CH_3)_2(C_6H_5)]_2$ (II). We have applied the procedure used by Green et al.[7] to protonate $(\pi\text{-}C_6H_6)MoL_3$ complexes. To a solution of 0.5 g of complexes I or II in 20 ml of ethanol was added 5 ml of concentrated hydrochloric acid. The solution was stirred for 10 min, giving a pale orange solution. Then a few drops of a saturated aqueous ammonium hexafluorophosphate solution was added. A yellow-orange powder precipitated which was collected, washed with water, and dried. It was also washed with pentane to eliminate any starting compound which might not have reacted. The yield was about 80% in the two cases. $[[\mu\text{-}(SCH_3)Fe(CO)_2P(CH_3)_3]_2H]^+PF_6^-$: yellow orange, mp 130 °C dec. Anal. Calcd: C, 23.37; H, 4.06; S, 10.39; F, 18.50; P, 15.10. Found: C, 23.42; H, 4.12; S, 10.28; F, 18.89; P, 15.08. $[[\mu\text{-}(SCH_3)Fe(CO)_2P(CH_3)_2C_6H_5]_2H]^+PF_6^-$: orange, mp 133 °C. Anal. Calcd: C, 35.67; H, 3.92; P, 12.57. Found: C, 35.68; H, 3.98; P, 12.56.

Protonation of $[\mu\text{-}(SCH_3)Fe(CO)_2P(C_6H_5)_2(CH_3)]_2$ (III) and $[\mu\text{-}(SCH_3)Fe(CO)_2P(C_6H_5)_3]_2$ (IV). The method described above did not give the protonated form. Protonation occurred, but the addition of aqueous solution of NH_4PF_6 precipitated only starting material.

We have tried to protonate III and IV in a mixture of CF_3COOH and HPF_6. After concentration, a mixture of III or IV and their protonated form was collected. Washing with benzene eliminated III or IV but drying the crystals under vacuum regenerated the unprotonated form. It was not possible to isolate the protonated compound in a pure state and we have observed it only by ir and NMR spectroscopic techniques on a solution of III or IV in a mixture of CH_2Cl_2 and CF_3COOH (1:1).

Results and Discussion

^{1}H NMR Spectra. (a) High-Field Region Resonance. All of the protonated products show a signal in the τ 25–27 range. This high-field resonance strongly suggests the hydride is in a bridging position. This is supported by the observations that in $H_2Fe_2[P(CF_3)_2]_2(CO)_6$, where the hydrides are terminal, hydride resonance occurs in the τ 15.6–15.8 range,[8] and on the other hand, in $HFe_3(CO)_{11}^-$, where the hydride bridges two iron atoms, resonance appears at τ 24.9.[9] This high-field resonance of bridging hydride compared to that of terminal hydride is a general trend of hydrido complexes of the same metal.[10] Moreover, the signal appears as a triplet when the number of phenyl groups in the phosphine is 0, 1, or 2. So the proton is equally coupled with the two phosphorus ligands. The coupling is quite small (4 Hz) but in the range found in $Os_3H(CO)_9[P(C_6H_5)_2(CH_3)]_3^+$.[11]

(b) Low-Field Resonance. The resonance of the methyl groups bonded to the phosphorus appears as a doublet and indicates that the two phosphorus ligands are equivalent. This resonance is shifted to lower field in comparison with the starting complexes.

The resonance of the methyl groups bonded to sulfur in the $[[\mu\text{-}(SCH_3)Fe(CO)_2P(CH_3)_{3-x}(C_6H_5)_x]_2H]^+$ complexes shows two triplets when $x = 0$, 1, and 2. As has been shown for the nonprotonated complexes,[3] each triplet can be considered the result of coupling between the methyl protons and the two phosphorus nuclei, but the splitting of triplets can result either from two slightly different positions for the two SCH_3 or from the coupling with the bridging hydride. For this reason, we have prepared the deuterated compound through the action of CF_3COOD and the SCH_3 resonance is now a single triplet (Figure 1). This confirms that the two triplets result from the coupling with the bridging hydride and that the two methyl groups are in syn positions.

In the case where $L = P(C_6H_5)_3$, the situation is more complex. When the spectrum is recorded immediately after the addition of trifluoroacetic acid, only one broad signal (τ 8.89) is observed for the SCH_3 groups. Then a second broad signal progressively appears (τ 8.72) and the first decreases in intensity. The evolution stops when the two signals are of equal intensity. In this case the phenomenon is attributed to the isomerization syn–anti (vide infra) of the two SCH_3 groups, as has recently been found in the nonprotonated complexes.[12]

Infrared Spectra. It has not been possible to detect the M–H stretching frequencies even by comparison of the infrared spectra of the protonated and deuterated complex. This can be the result of either a weak intensity of the band or an overlapping with the ligand frequencies occurring in the 1000-cm^{-1} area where the bridging hydrogen mode is expected.[10]

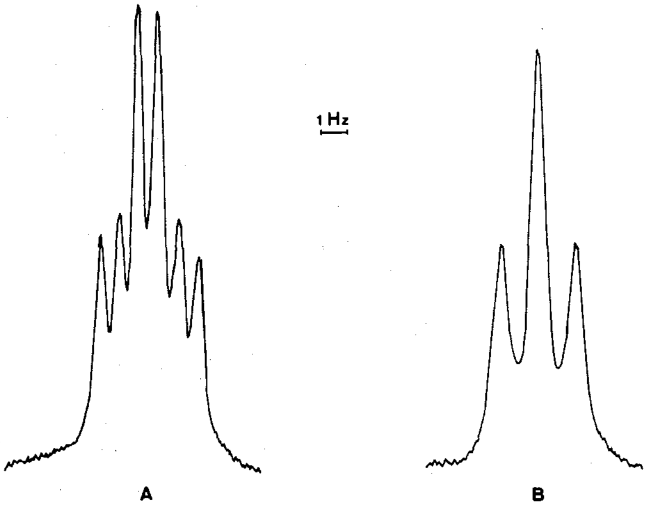

Figure 1. ^{1}H NMR spectra of the SCH_3 group in (A) $[[\mu\text{-}SCH_3\text{-}Fe(CO)_2P(CH_3)_2C_6H_5]_2H]^+$ and (B) $[[\mu\text{-}SCH_3Fe(CO)_2P(CH_3)_2\text{-}C_6H_5]_2D]^+$.

When $x = 0$, 1, or 2, the infrared spectra in the CO stretching region of the protonated species have the same pattern as that of the unprotonated complexes. It is only shifted by ca. 60 cm^{-1} to higher frequencies. As is expected, this shift decreases with the basicity of the ligand, so there is only a little difference between the CO stretching frequencies of the various protonated species. As the pattern of the CO stretching bands (number and relative intensities) is preserved, we may conclude that the C_{2v} point group of the unprotonated structure[3] is conserved when the protonation occurs: the two ligands L are trans to the metal–hydride–metal bond and the SCH_3 groups are syn disposed.

The examination of the results found with $L = P(C_6H_5)_3$ confirms the NMR observations. Immediately after the addition of trifluoroacetic acid, the infrared spectrum shows three CO stretching bands with the same pattern as the other complexes studied. Examination of the spectrum of the solution at equilibrium (as verified by NMR) shows three new bands with a different ratio of intensity, the least intense being the highest in frequency (Table I). Furthermore, if the trifluoroacetic acid is eliminated by high-vacuum evaporation, only the nonprotonated form is recovered. So we can be certain that this second product is also a protonated compound and what we have observed is a product of isomerization.

We have seen by proton NMR that this product has the two SCH_3 groups in an anti position. The fact that only three CO stretching frequencies are active strongly suggests that the local symmetry of the CO groups is preserved and indeed assumes that the configuration in the bridging atoms does not perturb the local symmetry. This hypothesis is supported by the close similarity of the infrared spectra of *syn*- and *anti*-$[Fe(SR)(CO)_3]_2$ in the CO stretching region[13] and also by observations on $Rh_2Cl(SR)(CO)_4$.[14] Therefore the ligands $P(C_6H_5)_3$ remain trans to the metal–hydride–metal bond.

Structure of the Protonated Species. The combination of the infrared and proton NMR results provides an insight into the structure of the $[[\mu\text{-}(SCH_3)Fe(CO)_2L]_2H]^+$ complexes. First, the position of the ligands is not affected by the protonation: they remain trans to the metal–hydrogen–metal bond. Second, except in the case where $L = P(C_6H_5)_3$, the SCH_3 bridges are syn disposed. However, one question remains. Are they directed toward the metal–hydrogen–metal bond (syn-endo) or in the opposite direction (syn-exo)?

In the nonprotonated species, the methyl groups are directed

Table I. Infrared and ^{1}H NMR Spectra

Compd	ν(CO),[a] cm^{-1}	τ(PCH$_3$),[b] ppm	*J*(P–CH),[d] Hz	τ(SCH$_3$),[d] ppm	*J*(P–SCH$_3$), Hz	*J*(H–SCH$_3$), Hz	τ(H), ppm	*J*(P–H), Hz
$[[\mu\text{-SCH}_3\text{Fe(CO)}_2\text{P(CH}_3)_3]_2\text{H}]^+\text{PF}_6^-$	2049 s 2029 m 1994 s	8.19	10 d	8.20 dt	1.3	0.6	25.6	4
$[[\mu\text{-SCH}_3\text{Fe(CO)}_2\text{P(CH}_3)_2\text{C}_6\text{H}_5]_2\text{H}]^+\text{PF}_6^-$	2049 s 2029 m 1996 s	7.89	10 d	8.58 dt	1.5	0.7	26.3	4
$[[\mu\text{-SCH}_3\text{Fe(CO)}_2\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{H}]^+\text{CF}_3\text{COO}^-$	2047 s 2028 m 1996 s	7.34	9.5 d	8.74 dt	1.3	0.7	26.6	4.4
$[[\mu\text{-SCH}_3\text{Fe(CO)}_2\text{P(C}_6\text{H}_5)_3]_2\text{H}]^+\text{CF}_3\text{COO}^-$	2046 s[c] 2026 m 1997 s			8.89	*e*	*e*	27.3	*e*
	2051 m[c] 2035 s 1996 s			8.89 8.72	*e*			

[a] Measured in CH$_2$Cl$_2$ solutions. [b] Measured in CH$_2$Cl$_2$ solutions with TMS internal reference. [c] See text. [d] Key: d, doublet; dt, doublet triplet. [e] Unresolved.

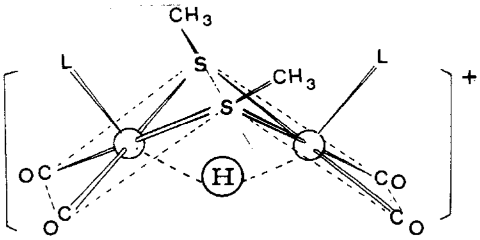

Figure 2. Proposed structure for $[[\mu\text{-SCH}_3\text{Fe(CO)}_2\text{L}]_2\text{H}]^+$ complexes.

toward the metal–metal bond and this is a consequence of the steric strains due to the sharp Fe–S–Fe angle.[15] However, the introduction of the proton probably induces an opening of this angle and some steric crowding in the metal–metal bond area. Moreover, the behavior of the protonated complex with L = P(C$_6$H$_5$)$_3$ could provide some arguments in favor of the syn-exo hypothesis. Indeed, with this ligand, we have observed the only case of syn → anti isomerization; this ligand is the most overcrowded of the series and it is only when the bridges are syn-exo that this overcrowding can interfere with the bridge positions. So we suggest that the molecule has the structure syn-exo (Figure 2). However this isomerization could be the result of a more subtle electronic or steric effect and the structure with the SCH$_3$ groups in the syn-endo position cannot be definitively excluded.

Nucleophilicity of the Metal–Metal Bond and Donor Properties of the Phosphorus Ligands. From the Experimental Section, we have seen that the behaviors of complexes are quite different when x = 0, 1 or when x = 2, 3. In the first case, protonation gives stable and isolable materials. In the latter case, protonated species cannot be isolated. Moreover, when the trifluoroacetic acid is eliminated, only the starting material is recovered. These results are consistent with the observations concerning the protonation of mononuclear carbonyls; i.e., replacement of carbonyl group by phosphines increases the metal basicity.[16] However in our case the effect of a variation of basicity of ligand seems more pronounced because only a slight modification as the replacement of P(CH$_3$)$_2$C$_6$H$_5$ by PCH$_3$(C$_6$H$_5$)$_2$ induces a great change in the behavior of complexes toward the proton. This is certainly the result of the position of the ligands L trans to the metal–metal bond.

Registry No. I, 58150-42-8; II, 34215-24-2; III, 58150-43-9; IV, 31340-71-3; $[[\mu\text{-(SCH}_3)\text{Fe(CO)}_2\text{P(CH}_3)_3]_2\text{H}]^+\text{PF}_6^-$, 58150-45-1; $[[\mu\text{-(SCH}_3)\text{Fe(CO)}_2\text{P(CH}_3)_2\text{C}_6\text{H}_5]_2\text{H}]^+\text{PF}_6^-$, 58150-47-3; $[[\mu\text{-(SCH}_3)\text{Fe(CO)}_2\text{PCH}_3(\text{C}_6\text{H}_5)_2]_2\text{H}]^+\text{CF}_3\text{COO}^-$, 58150-49-5; $[[\mu\text{-(SCH}_3)\text{Fe(CO)}_2\text{P(C}_6\text{H}_5)_3]_2\text{H}]^+\text{CF}_3\text{COO}^-$, 58150-51-9.

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Effect of Chelate Ring Size on Boron Substitution Reactions. Complexation of Phenylboronic Acid with Malonic Acid

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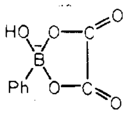
We reported recently[1] on the reaction of phenylboronic acid, PhB(OH)$_2$, with oxalic acid to form the tetrahedral anionic complex I. The kinetic results are unusual from the point



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of view of normal substitution processes in that ligand donor atom protonation is required for successful reaction, the more protonated ligands reacting more rapidly. On reaction, boron undergoes a change in coordination number from 3 (sp^2) to 4 (sp^3). One ligand donor atom occupies the fourth coor-