Stereochemical Nonrigidity of Protonated Pseudotetrahedral Organotransition Metal Complexes

Thomas C. Flood,* Edward Rosenberg, and Ahmad Sarhangi

Contribution from the Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90007. Received November 29, 1976

Abstract: The complexes (arene)M$(CO)_2(PPhMe_2)$ (arene = benzene and mesitylene; M = Cr, Mo, and W) and $(\eta^5\text{-}C_5H_4R)$-$Mn(CO)_2(PPhMe_2)$ (R = H and CH_3) are quantitatively protonated at the metal by a four-tenfold molar excess of CF_3SO_3H. In every case, NMR spectroscopy detects two isomers which undergo rapid nondissociative interconversion. Complete line shape analysis reveals $\Delta G^{\ddagger}$ values for this interconversion in the range of 11-15 kcal/mol. The proton therefore occupies a coordination site, changes the geometry to a probable square pyramid, and renders the complex fluxional. Nevertheless ^{13}C NMR of (mesitylene)$Cr(CO)_2(PPhBzMe)H^+$ shows that the two carbonyl ligands are not undergoing mutual site exchange, and neither are the carbonyl ligands of the isoelectronic neutral complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPhBzMe)H$ exchanging sites. Several mechanistic models for the stereochemical lability of these molecules are discussed.

Pseudotetrahedral molecules of the type (η^6-arene or η^5-C_5H_5)MLL′L″ are configurationally stable in the absence of ligand dissociation.[1] However, it has been found in several different laboratories that resolved iron alkyls CpFe(CO)-(PPh_3)R (Cp ≡ η^5-C_5H_5) are partially racemized in the presence of electrophiles.[2-4] In order to examine the stereochemical effects of electron deficient species on the geometry and configurational stability of pseudotetrahedral molecules, we have undertaken the study of the interaction of electrophiles with these molecules where M = Cr, Mo, W, and Mn, and L = phosphine or CO.

While it has been known for many years that (η^6-C_6H_6)-$Cr(CO)_3$, for example, may be metal protonated,[5] only recently have questions been raised concerning the detailed structure of the resultant cation.[6] It has been shown that CpMn-$(CO)_{3-n}L_n$ and (arene)$Cr(CO)_{3-n}L_n$ (L = phosphine or phosphite; arene = benzene, toluene, etc.; n = 1, 2) are also metal protonated, and the NMR data given were interpreted in every case in terms of a single geometrical isomer although no convincing evidence for molecular geometry has been presented.[6,7] Since there is extensive evidence now that neutral pentacoordinate[10,11] and pseudopentacoordinate[12-14] complexes are configurationally labile, often with low activation barriers, it seemed likely that the isoelectronic protonated molecules under consideration might have more than one isomer, and might be configurationally labile. The following describes our efforts to define the geometry and the pathways of rearrangement of electrophile adducts of pseudotetrahedral molecules.

Results

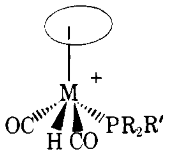
Intermolecular Proton Exchange.[15] Titration of (η^6-$C_6H_3Me_3$)$Cr(CO)_2(PPhMe_2)$ (**2**) with CF_3CO_2H in $CDCl_3$ led to changes in its ^{1}H NMR spectrum, until at a **2**:CF_3CO_2H ratio of 1:20, none of the resonances showed any further change with additional acid. At that point, intermolecular proton exchange was slow since all resonances were sharp. The mesitylene ring proton resonance of **2** itself appeared at δ 4.33 ppm, while for totally protonated **2**·H^+, the same resonance was at δ 6.00 ppm. The percent of protonated material could thereby be determined directly, and half-protonation was achieved at ca. 3.5-fold excess of acid. **2**·H^+ is therefore only slightly more acidic than CF_3CO_2H in chlorocarbon solvents.

A similar titration was performed on **2** using CF_3SO_3H in CD_2Cl_2. Protonation of **2** was essentially complete after less than a twofold excess of acid was added, and slow exchange was reached at ca. a fourfold excess. Chemical shifts for the entire spectrum of **2**·H^+ were the same with either CF_3CO_2H or CF_3SO_3H, indicating no pronounced dependence of the properties of the cation on the nature of the counterion.

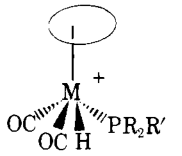
Titration of (η^5-$C_5H_4CH_3$)$Mn(CO)_2(PPhMe_2)$ (**6**) with CF_3CO_2H in $CDCl_3$ revealed that intermolecular proton exchange was much faster for this apparently less basic compound. Protonation was complete at an H^+:**6** ratio of 8:1, but the metal hydride resonance only became sharp after a 30-fold excess of the acid had been added (δ_{MH} −5.4, $^2J_{^1H^{31}P}$ = 47 Hz). Titration of **6** with CF_3SO_3H showed that protonation was complete at about a twofold excess of acid, and the slow exchange limit was attained at a sixfold excess.

Intramolecular Isomerization: Symmetrical Phosphine. ^{1}H NMR spectra of compounds **1**-**6** (Table I) at 22 °C in chlorocarbon solvents in the presence of a four-sixfold molar excess of CF_3SO_3H revealed sharp arene (or Cp) and methyl singlets, and sharp hydride doublets in the range of δ −5 to −7 ppm with $^2J_{PH}$ = 20 to 70 Hz.

At temperatures from −50 to −86 °C, limiting NMR spectra were obtained which in all cases were consistent with the presence of two isomers (e.g., Figure 1): two arene singlets, two sets of P-CH_3 resonances, and two hydride doublets with $^2J_{PH}$ of 50-75 Hz. The P-CH_3 resonances are particularly informative. In cases where they are not obscured by mesitylene methyl resonances, one observes one doublet for the first isomer and two doublets for the second isomer. These observations are consistent with trans and cis square-pyramidal geometries, respectively, as in **12t** and **12c** (see the Discussion).



12t



12c

Since **12t** has a plane of symmetry containing the phosphine, the two phosphine methyl groups are equivalent, giving rise to one doublet in the ^{1}H NMR. Since the metal in **12c** is chiral, the phosphine methyl groups are diastereotopic and exhibit two distinct sets of doublet resonances.[16] Hence the hydride trans to phosphorus has $^2J_{PH}$ of 20-30 Hz and that cis to phosphorus has $^2J_{PH}$ of 50-75 Hz.

As the sample is warmed above the low temperature limit, the ^{1}H NMR spectra of these protonated species broaden and coalesce until at some temperature between 25 and 50 °C, high temperature limiting spectra are reached wherein the hydride is a single doublet whose $^2J_{PH}$ is the weighted average of the two doublets observed at the low temperature limit. Since coupling is maintained throughout the temperature range, the

Table I. Proton NMR Data for Metal-Protonated and Neutral Hydride Complexes

Compound[a]	δ_{ppm} (Me_4Si)	J_{PH}, Hz (av)[b]	$\Delta G^{\ddagger}_{c-t}$, kcal/mol[d]	% cis[b]	J_{PH}, Hz[j] Cis	Trans
$(C_6H_6)Cr(CO)_2(PPhMe_2)\cdot H^+$ (**1**·H+)	−5.4	50	12.5 ± 0.3[e]	47	75	28
(mes)$Cr(CO)_2(PPhMe_2)\cdot H^+$ (**2**·H+)	−5.5	66	13.1 ± 0.4	83	68	26
(mes)$Mo(CO)_2(PPhMe_2)\cdot H^+$ (**3**·H+)	−5.7	32	12.2 ± 0.4	30	58	21
(mes)$W(CO)_2(PPhMe_2)\cdot H^+$ (**4**·H+)	−7.2	30	12.6 ± 0.5	18	63	22
$(C_5H_5)Mn(CO)_2(PPhMe_2)\cdot H^+$ (**5**·H+)	−5.5	—	15.1 ± 0.6[f]	72[h]	52	23
$(C_5H_4Me)Mn(CO)_2(PPhMe_2)\cdot H^+$ (**6**·H+)	−5.4	47[c]	14.2 ± 0.4	77[c]	54	24
$(C_6H_6)Cr(CO)_2(PPhBzMe)\cdot H^+$ (**7**·H+)	—	—	—	—	—	—
(mes)$Cr(CO)_2(PPhBzMe)\cdot H^+$ (**8**·H+)	−5.1	64	—	76 (19)[i]	78 (72)[i]	25
(mes)$Mo(CO)_2(PPhBzMe)\cdot H^+$ (**9**·H+)	−6.1	33	—	25[i]	54	21
$(C_5H_5)Mo(CO)_2(PPhBzMe)H$ (**10**)	−5.9	51	13.3 ± 0.6[g]	76[i]	—	—
$(C_5H_5)Fe(CO)(PPhBzMe)H$ (**11**)	−13.0[k]	77	—	—	—	—

[a] Counterion is $CF_3SO_3^-$; mes = mesitylene; solvent was CD_2Cl_2; concentrations of complex ranged from 0.10 to 0.16 M; acid was present in 4 to 6 M excess for Cr, Mo, and W complexes, and 8 to 10 M excess for Mn complexes. [b] At 22 °C. [c] At 55 °C. [d] Calcd at 25 °C using line shape analysis of the hydride and/or Cp or arene resonances. [e] $\Delta G^{\ddagger}_{cis-cis}$ = 12.0 ± 0.5 kcal/mol from line shape analysis of $P-CH_3$ ^1H NMR resonances. [f] $\Delta G^{\ddagger}_{cis-cis}$ = 11.6 ± 1.0 kcal/mol from line shape analysis of $P-CH_3$ ^1H NMR resonances. [g] $\Delta G^{\ddagger}_{cis-cis}$ = 11.7 ± 0.6 kcal/mol from line shape analysis of the ^{13}CO resonances. [h] At −40 °C. [i] Of both cis diastereomers, ( ) is the percent of minor cis isomer. [j] At −40 to −80 °C. [k] $\Delta\delta$ for diastereotopic hydride resonances = 0.43 ppm.

cis–trans rearrangement is nondissociative in hydride and phosphine. Chromium complex **2** was prepared with ca. 10% ^{13}C enrichment in the CO ligands. Ambient temperature ^{13}C NMR of enriched **2**·H+ revealed a single phosphorus-coupled CO resonance further substantiating the nonrigidity of the species, and also showing that the CO ligands are not dissociating on the NMR time scale. At −80 °C, the ^{13}C NMR spectrum of the CO ligands of **2**·H+ is as shown in Figure 2. The coupling constants shown were confirmed using the cis/trans ratio obtained from ^1H NMR, calculation of the high temperature limiting $^2J_{PC}$, and comparison with the observed value.

Computer simulation of the Cp or arene ring proton and/or hydride resonances using a simple two-site intramolecular exchange mechanism yields good fits with observed spectra. Calculated $\Delta G^{\ddagger}$ values (at 25 °C) for the cis to trans isomerization are shown in Table I.

The temperature dependent ^1H NMR of **1**·H+ and **5**·H+ (Figures **1** and 3) show the onset of averaging of the diastereotopic cis isomer (**12c**) phosphine methyl resonances at lower temperatures than the onset of cis–trans interchange. Good fits of simulated spectra to observed spectra are obtained by treating the phosphine methyl resonances as a three-site exchange with two rate constants. Calculated activation parameters are shown in Table I.

Attempts to Use Other Electrophiles. Interactions of HgX_2[17] (X = I, Br, Cl), BX_3 (X = Cl, Br), $AlCl_3$, and I_2[18] with **1–3**, **5**, and **6** were also examined, and led to either insoluble complexes, or decomposition except in the case of molybdenum complex **3** with excess $HgBr_2$ which was well-enough behaved and soluble enough in acetone-d_6 to yield NMR spectra. The ^1H NMR spectrum revealed no free **3**, and the mesitylene ring proton resonance, normally at δ 4.5 ppm, was shifted to δ 6.38 ppm. Added free mesitylene exhibited a separate resonance at δ 6.8 ppm. The spectrum is independent of temperature in the range of −90 to +40 °C except that at low temperature the $P-CH_3$ and arene-CH_3 resonances shift slightly and become overlapping. The ^{31}P NMR (proton-decoupled) spectrum of the $HgBr_2$ complex contains one sharp singlet.

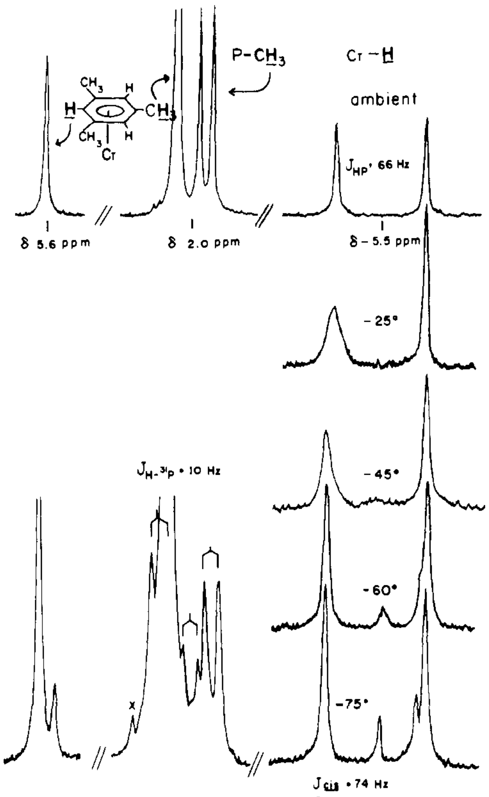


Figure 1. Variable temperature ^1H NMR spectrum of $[(mesitylene)Cr(CO)_2(PPhMe_2)H]^{+-}O_3SCF_3$ (**2**·H+) in CD_2Cl_2. Intensities are not to scale, and Ph resonances are not shown.

Protonated Complexes Containing Chiral Phosphine. In order to obtain more information concerning the nature of the nondissociative rearrangement pathways exhibited by **1**·H+–**6**·H+, the symmetry of the pseudotetrahedral molecules was removed by incorporating chiral but racemic methylphenylbenzylphosphine to form $(C_6H_6)Cr(CO)_2(PBzPhMe)$ (**7**) and (mes)$M(CO)_2(PBzPhMe)$ (M = Cr is **8**, M = Mo is **9**). Also, for purposes of comparison, the two neutral complexes $CpMo(CO)_2(PBzPhMe)H$ (**10**) and $CpFe(CO)(PBzPhMe)H$ (**11**) were prepared and their spectra examined. Compounds **7–10** were enriched in ^{13}CO by ca. 10%. As shown for **8** in Figure 4a, the presence of the chiral phosphine renders the two CO ligands diastereotopic and distinct in the ^{13}C NMR. If interaction with an electrophile were to result in nonrigidity which mutually exchanged the two CO sites of **1**·H+–**9**·H+, one would see only a single doublet for the ^{13}CO ligands in the fast cis–trans isomerization limit of the ^{13}C NMR spectrum. But if the rearrangement of **1**·H+–**9**·H+ and **10** did not involve mutual CO site exchange, then two distinct ^{13}CO doublets

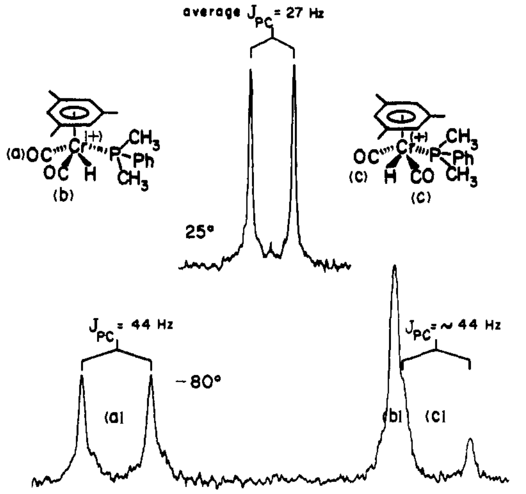


Figure 2. ^{13}C NMR spectrum of the CO ligands of [(mesitylene)-Cr(CO)$_2$(PPhMe$_2$)H]$^+$$^-O_3SCF_3$ (**2**·H$^+$) in CD$_2$Cl$_2$ at 25 and at −80 °C.

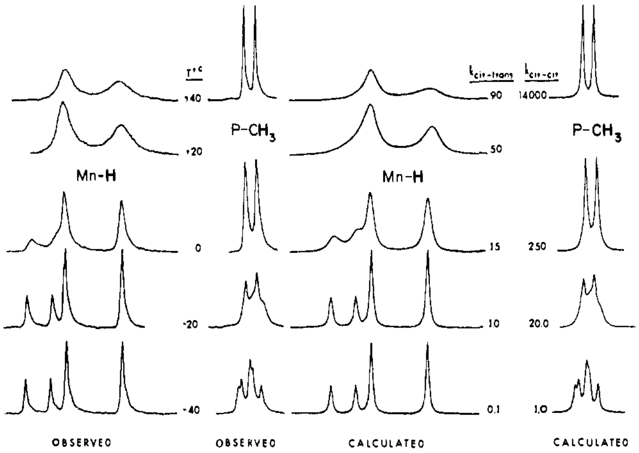


Figure 3. Variale temperature ^{1}H NMR spectra and calculated spectra for [CpMn(CO)$_2$(PPhMe$_2$)H]$^+$$^-O_3SCF_3$ (**5**·H$^+$) in CDCl$_3$. Ph and Cp resonances are not shown.

would be observed for **7**·H$^+$–**9**·H$^+$ and **10** in the limit of fast isomerization.

Protonation of either **7** or **8** under the same conditions used for **1**–**6** led to the ^{13}C NMR spectra shown for **8**·H$^+$ in Figure 4. The observation of two doublets in both cases (overlapping in the case of **7**·H$^+$) establishes that on the NMR time scale the two CO ligands are not site exchanged. In each case, the two doublets observed have different values of $^2J_{PC}$, which is readily explained by noting that the two cis diastereomers of **7**·H$^+$, **8**·H$^+$, or **9**·H$^+$ will have different populations. Equation 1, for example, shows the three diastereomers of **8**·H$^+$, and Figure 4d shows the ^{13}C NMR spectrum of their CO ligands at −90 °C, with assignments as indicated by letters (a–f) based on the ^{13}C spectrum of **2**·H$^+$ (Figure 2). The ratio of trans: cis:cis calculated from this and the ^{1}H spectrum is 24:57:19.

^{13}C NMR spectra of **8**·H$^+$ in 2:1 CF$_3$CO$_2$H–CDCl$_3$ at 22 °C were also examined. These conditions were similar to those used by previous workers who claimed that (arene)Cr-(CO)$_2$(PR$_3$)·H$^+$ species exist as a static cis isomer.[6] The ^{13}CO spectrum was identical with the spectrum of **8**·H$^+$ CF$_3$SO$_3$$^-$, which indicates the presence of a substantial mole fraction of trans isomer with the CF$_3$CO$_2$$^-$ counterion as well, and shows no obvious effect of the counterion on the mechanism of geometrical lability. Protonation of the molybdenum complex **9** leads to a ^{13}CO spectrum which contains two sharp doublets at −80 °C, as shown in Figure 5c, which have equal coupling

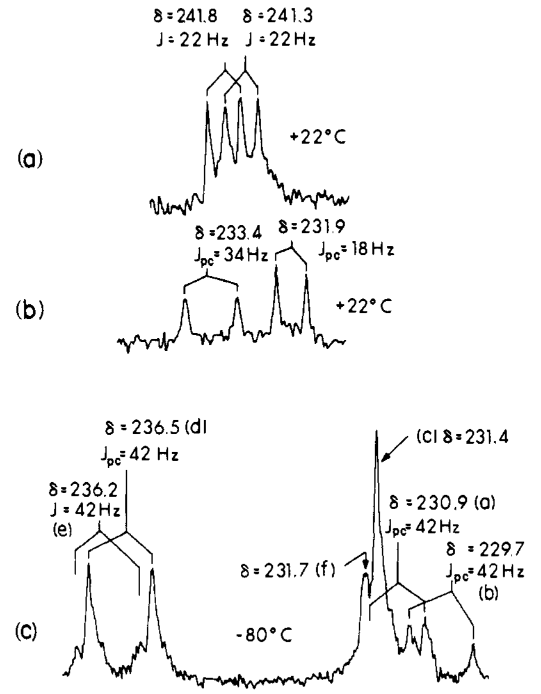
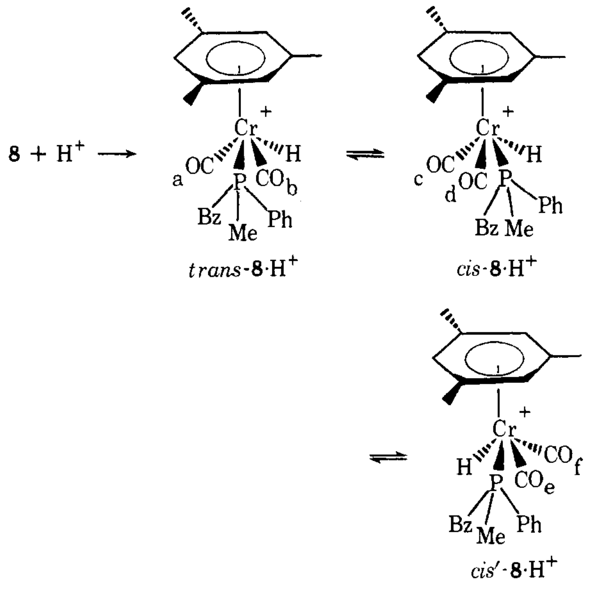


Figure 4. ^{13}C NMR spectra of the CO ligands of (a) (mesitylene)-Cr(CO)$_2$(PPhBzMe) (**8**), (b) **8**·H$^+$$^-O_3SCF_3$ at 22 °C, and (c) **8**·H$^+$$^-O_3SCF_3$ at −80 °C. See eq 1 in the text for peak assignments of (c).



(1)

constants. This is consistent with the predominance of the trans isomer of **9**·H$^+$, as is the ^{1}H NMR spectrum which reveals only a small amount of cis isomer in CD$_2$Cl$_2$ at −80 °C. At +22 °C, however, a calculated ratio of trans:cis of 4:1 is obtained from the ^{1}H NMR $^2J_{PH}$ of the metal hydride, and the ^{13}C NMR shows two doublets with different phosphorus coupling, indicating also that two cis diastereomers of unequal population are now making a significant contribution to the average spectrum. The isomerization process in the case of molybdenum, as with chromium, is not leading to CO site exchange.

The ^{13}CO NMR of **9** in a saturated solution of HgBr$_2$ in acetone-d_6 at +22 °C shows a spectrum very similar to that of **9**·H$^+$ at −80 °C (Figure 5d). Taken along with the observation of one ^{31}P NMR signal for **3**·(HgBr$_2$)$_n$, the ^{13}C NMR data suggest the presence of only the trans isomer, and therefore, no information on stereochemical nonrigidity can be obtained.

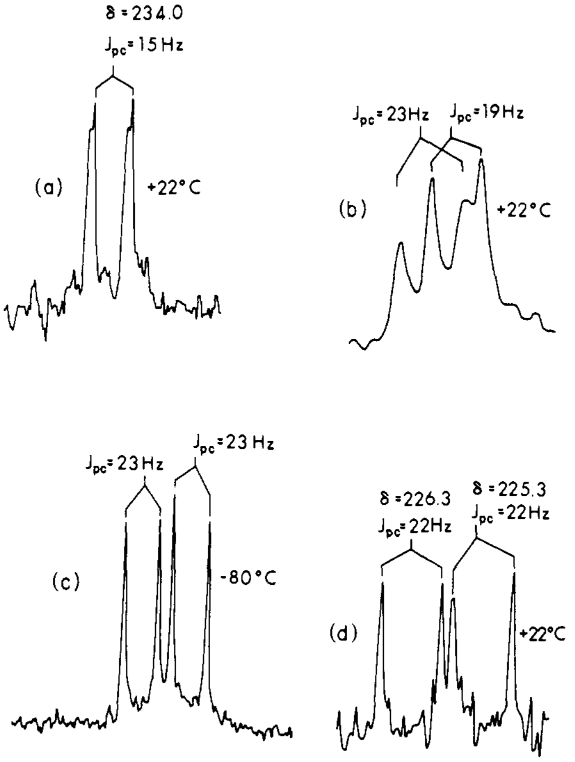


Figure 5. ^{13}C NMR spectra of the CO ligands of (a) (mesitylene)-$Mo(CO)_2(PPhBzMe)$ (**9**) at 22 °C, (b) **9**·$H^{+-}O_3SCF_3$ at 22 °C, (c) **9**·$H^{+-}O_3SCF_3$ at −80 °C, and (d) **9**·$(HgBr_2)_n$ at 22 °C.

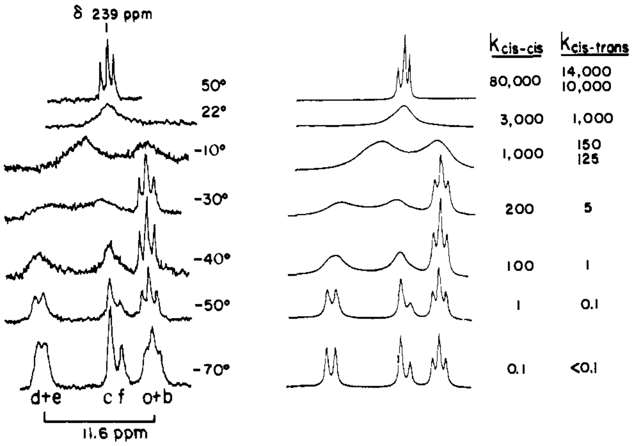


Figure 6. ^{13}C NMR spectra of the CO ligands of $CpMo(CO)_2$-$(PPhBzMe)H$, and calculated spectra. Assignments (a–f) are as in eq 1 in the text.

The ^{13}CO NMR spectrum of $CpMo(CO)_2(PBzPhMe)H$ (**10**) was examined from −70 to +75 °C (Figure 6) so that the mechanism of cis–trans isomerization of **10** could be compared with those of the isostructural protonated molecules. The spectrum at −50 °C can be assigned by comparison with the limiting spectra of **2**·H^+ (Figure 2) and **8**·H^+ (Figure 4c), and the peaks are lettered (a–f) in analogy with the assignments made in eq 1 and Figure 4c. Broadening of several peaks at −70 °C in Figure 6 probably arises from the onset of freezing out phosphine rotamers.[19] Compound **10** behaves very similarly to **1**·H^+ and **5**·H^+ in that resonances (c–f) of the cis isomers coalesce at lower temperature than do resonances (a) and (b) of the trans isomer, indicating that cis–cis isomerization is faster than cis–trans. Calculated spectra are also shown in Figure 6. Activation parameters calculated were $\Delta G^{\ddagger}$ cis–cis = 11.7 ± 0.6 kcal/mol and $\Delta G^{\ddagger}$ cis–trans = 13.3 ± 0.6 kcal/mol.

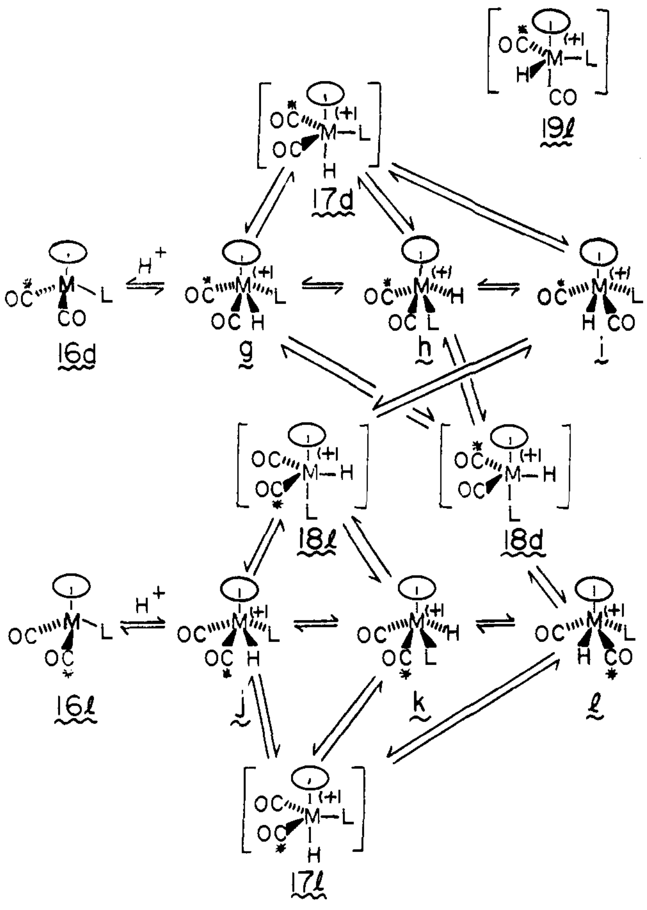
Finally, since it has been reported that the two diastereotopic phosphine methyl groups of $CpFe(CO)(PPhMe_2)H$ exhibit a single ^{1}H NMR doublet,[20] we examined the ^{1}H NMR of $CpFe(CO)(PBzPhMe)H$ (**11**). The proton spectrum of **11** revealed two hydride doublets (Table I).

Discussion

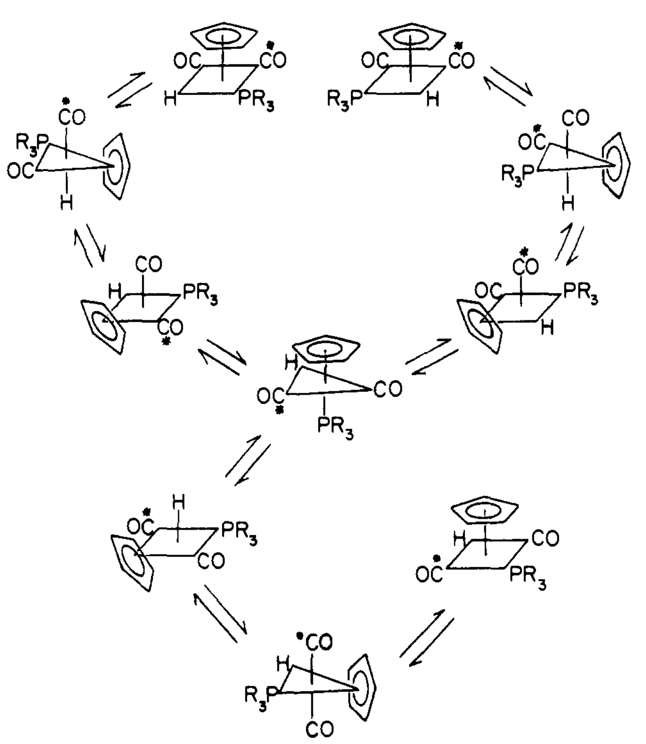
Three basic idealized geometries for the adduct of an electrophile with a pseudotetrahedral molecule can be imagined. It is significant that in every case we have examined where the proton is the electrophile, two and only two isomers have been observed. In four cases where the methyl resonances of the dimethylphenylphosphine ligand were not obscured, it was shown that one of the two isomers is chiral. These observations suggest that the geometry of the protonated complexes is most nearly approximated by a square pyramid, as in **12**, rather than a protonated pseudotetrahedron (three isomers, one chiral) or a trigonal bipyramid (seven isomers, three chiral). Further corroboration of this conclusion lies in the extensive analogy which has become apparent in our work between **1**·H^+–**9**·H^+ and the neutral isoelectronic molybdenum molecules which have been thoroughly studied by Faller and Anderson,[12] and which are most nearly represented by a square-pyramidal idealized geometry. The behavior of **1**·H^+–**9**·H^+ taken as a whole is therefore more consistent with pseudosquare-pyramidal geometry than any other, with the corollary that the hydride is able to sterically compete with the other three basal ligands thus leading to geometric distortions of the original pseudotetrahedron to form its own distinct coordination site. Also, the stereochemical lability exhibited by these species must be a function of the pseudopentacoordination and not a property of the hydride ligand since $CpFe(CO)(PPhBzMe)H$ (**11**) is stereochemically rigid.

Since the behavior of these protonated species is so analogous to that of neutral pseudosquare-pyramidal molecules, the analysis of Faller and Anderson[12] serves as a starting point for mechanistic interpretation. In this analysis the assumption is made that cis–cis and cis–trans rearrangements proceed via a trigonal-bipyramidal intermediate or transition state in which the cyclopentadienyl ligand always occupies one axial position. A trigonal-bipyramidal intermediate is formed by moving one of the four basal ligands directly to the second axial site and rearranging the other three in a "least motion" type of path. Applying this formalism to our system generates three possible intermediates, **17**, **18**, and **19**, shown in Scheme I. By incorporating a chiral phosphine, the two CO ligands become distinguishable, and therefore, **g**, **h**, and **i** are distinguishable from **i**, **k**, and **l**. We have shown under conditions of rapid intramolecular rearrangement but slow intermolecular proton transfer that the two CO ligands remain distinct on the NMR time scale (vide supra). This means that trigonal bipyramid **19** cannot be an intermediate in the rearrangement because it would exchange the sites of the two CO ligands. Intermediate **17d**, wherein hydride is axial, would interconvert **g**, **h**, and **i** (and **17l** would interconvert **j**, **k**, and **l**) but **g**, **h**, and **i** would remain distinct from **i**, **k**, and **l**. This is consistent with the observed data. On the other hand, **18l**, wherein phosphine is axial, would interconvert **i**, **j**, and **k** (and **18d** would interconvert **g**, **h**, and **l**) but **i**, **j**, and **k** would remain distinct from **g**, **h**, and **l**. This is also consistent with the data in the limit of slow intermolecular proton exchange. If *both* **17** and **18** were present as intermediates, since these interconvert sets of isomers which are not mutually exclusive, all six isomers would be averaged, and one CO doublet would be observed, contrary to our results. It can be said with certainty, accepting this mechanistic model, that *either* the hydride *or* the phosphine may become axial in the intermediate, but not both. Also, the CO ligand does not

Scheme I



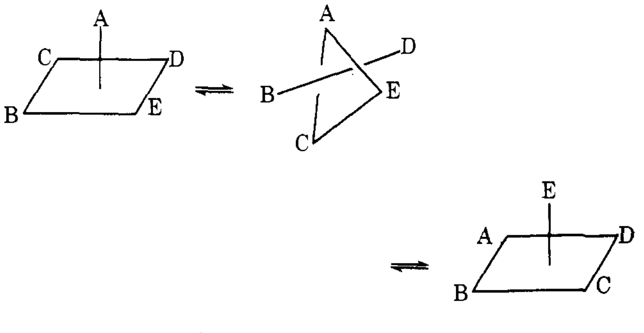
Scheme II



become axial on the NMR time scale. This argument applies equally to $1\cdot H^+$–$9\cdot H^+$ and **10**, and is a conclusion which could not previously be drawn from the more symmetrical neutral systems which were studied.

In principle, one might distinguish between the two possible intermediates. If **17** is the intermediate, intermolecular proton transfer at rates slightly slower than the intramolecular process would not interconvert **16d** and **16l**. If **18** is the intermediate, intermolecular proton exchange will interconvert **16d** and **16l** (provided that intermolecular exchange occurs from both the cis and trans protonated forms). Unfortunately, under conditions of intermolecular exchange using a variety of M:H$^+$ ratios, we have not been able to obtain sharp limiting spectra. Attempts at heating the solutions to temperatures of 50 °C or above led to rapid decomposition of the sample.

It should be pointed out that other mechanistic models can be constructed which account for these arrangements. For example, the well-known Berry pseudorotation (BPR) forms the basis of a usable model. One may envisage the process which is the reverse of the usual BPR in that the 20 possible trigonal bipyramids are viewed as intermediates interconverting 30 possible square pyramids. If the assumptions are made on steric grounds that (a) the arene and phosphine ligands may not be one axial and the other equatorial (they may both be axial or both equatorial) in the trigonal bipyramid and (b) the arene may be basal in the square pyramid, but the arene and phosphine may not be cis to each other in the base, then examination of a geometrical representation of the complete set of pseudorotations[24] allows one to immediately reduce the set of possible isomerizations to that shown in Scheme II and the mirror image of Scheme II. The Berry pseudorotational model with the above arbitrary but sterically reasonable constraints is therefore identical with the case where *only* phosphine assumes an axial position in the intermediate in the Faller–Anderson model, except that the BPR model entails six additional intermediates. However, the Fallern–Anderson and the BPR models cannot be distinguished from extant data, and there are undoubtedly other mechanistic models which could be generated as well.



All of our data, and that of other workers[12,13] on neutral pseudosquare-pyramidal systems, are most consistent with a mechanism (using the Faller–Anderson model) wherein the phosphine assumes the second axial position. In our cationic systems, this would mean that a chiral metal would racemize *if* proton transfer were slower than the intramolecular isomerization and if rates of intermolecular proton transfer between cis and trans protonated forms were comparable. Whether these conditions actually obtain remains to be demonstrated, presumably by racemization studies of resolved complexes. Not enough is known as yet to determine whether the patterns of motion in compounds as diverse as $CpMn(CO)_2L\cdot H^+$, $CpMo(CO)_2LX$, $CpMo(CO)L_2X$,[13] and (arene)M$(CO)_2L\cdot H^+$ will be described by a simple set of empirical rules, or whether there will be a family of permutational paths which are close to one another in energy, and therefore, are subject to control by highly subtle factors.

Experimental Section

General. All reactions were carried out in flamed-out glassware under an atmosphere of prepurified nitrogen. THF was distilled from a purple solution of benzophenone dianion just before use. All other solvents were degassed by vigorously bubbling prepurified nitrogen through them. Melting points (Thomas-Hoover apparatus) and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrophotometer. Preparative photochemical reactions were carried out using an Hanovia 450-W medium pressure mercury arc lamp either in a quartz immersion apparatus, or by external irradiation of a Pyrex round bottomed reaction vessel. Microanalyses were performed by Elek Microanalytical Laboratories, Torrance, Calif.

$CpMn(CO)_3$ and $(MeCp)Mn(CO)_3$ were purchased, and (benzene)$Cr(CO)_3$, (mesitylene)$M(CO)_3$ (M = Cr, Mo, W), $CpFe(CO)_2I$, $CpMo(CO)_3I$, $PPhMe_2$, and PBzPhMe were all prepared by standard procedures. Samples of (benzene)$Cr(CO)_3$, (mesitylene)$Cr(CO)_3$, $CpMo(CO)_3I$, and (mesitylene)$Mo(CO)_3$ were enriched by ca. 10–15% ^{13}C in the CO ligands by external photolysis of these materials in benzene solution by the Hanovia mercury arc lamp through Pyrex and under ^{13}CO (90% ^{13}C) atmosphere.

NMR Spectra. ^1H, ^{13}C, and ^{31}P NMR were measured on a Varian XL-100 NMR spectrometer. The temperature of the probe was monitored with a Varian temperature control unit which was calibrated with a standard thermocouple. Errors in reported temperatures are ±2 °C at a maximum. Values of δ for ^1H and ^{13}C spectra are reported positive downfield with respect to internal Me_4Si except in samples containing CF_3SO_3H where the solvent was used as an internal reference and then converted to δ values. Coupling constants in ^{13}C spectra are reported to ±2 Hz, and ±1 Hz for ^1H NMR spectra. All samples were prepared udder N_2 atmosphere using degassed CD_2Cl_2, $CDCl_3$, or $CD_3C_6D_5$, and freshly distilled CF_3SO_3H or CF_3COOH. ^1H spectra were run in 5-mm tubes either sealed under vacuum or septum stoppered with all transfers done by distillation or by syringe. ^{13}C NMR samples were filtered while loading into 12-mm tubes under inert atmosphere.

Line-Shape Analysis and Activation Parameter Calculations. Computer simulation of ^1H NMR spectra was performed using DNMR 4.[22] Changes in population with temperature were calculated for intramolecular rearrangements by assuming $\Delta S = 0$; i.e., ΔG is constant over the temperature range studied. Changes in population were then calculated from $\log K_2 = (T_1/T_2) \log K_1$ (K = (cis/trans)). The above assumption was verified for **5**·H^+ and **10** by measuring the changes in cis/trans at three temperatures below the low temperature limit and reasonable agreement was obtained (±0.03). The rate constants obtained from the line shape analysis were used in a weighted least-squares program to calculate $\Delta G^{\ddagger}$ and the Arrhenius parameters. Standard deviations of ±0.5 kcal were obtained in most cases using at least five rate constants at different temperatures.

Preparation of Compounds 1–9. 1–3 and **7–9** were all prepared in essentially the same manner. For example, to prepare **3**, a solution of (mes)$Mo(CO)_3$ (3 g) and $PPhMe_2$ (2 g) in 300 mL of ether was irradiated for 3 h in the immersion apparatus (Pyrex filter), during which the entire apparatus was kept in an ice-salt water mixture to minimize the thermal reaction leading to arene displacement by phosphine. After solvent evaporation, the residue was chromatographed (alumina, hexane). Elution with hexane, hexane-benzene (1:1), and finally benzene led to isolation of the orange product **3** which was crystallized from hexane, 3.3 g (80%), mp 94–96 °C. When the photolysis was carried out in benzene, very little of the desired product was obtained: IR ν_{CO} 1865, 1805 cm^{-1}; NMR ($CDCl_3$) δ 1.53 (d, J_{PH} = 10 Hz, 6 H), 2.13 (s, 9 H), 4.72 (s, 3 H), 7.33 ppm (m, 5 H). Anal. Calcd for $C_{19}H_{23}MoO_3P$: C, 55.62; H, 5.65. Found: C, 55.46; H, 5.59. Data for other compounds follow. **1:** $(C_6H_6)Cr(CO)_3$ (1.1 g) and 1.0 g of $PPhMe_2$ in 25 mL of benzene was irradiated externally for 2 h. Product was eluted from an alumina column using 1:1 hexane:benzene, recrystallized from hexane–benzene, mp 130–133 °C, 400 mg (25%), yellow-orange crystals: IR ($CHCl_3$) 1910, 1845 cm^{-1} ($\nu_{C\equiv O}$); NMR ($CDCl_3$) δ 1.52 (d, J_{PH} = 9 Hz, 6 H), 4.50 (s, 6 H), and 7.40 ppm (m, 5 H). Anal. Calcd for $C_{16}H_{17}CrO_2P$: C, 59.26; H, 5.28. Found: C, 59.42; H, 5.25. **2:** (mes)$Cr(CO)_3$ (5.1 g) and $PPhMe_2$ (5.5 g) in 150 mL of benzene were irradiated externally for 12 h. Product was eluted from an alumina column using 9:1 hexane:ethyl acetate. Recrystallization from hexane gave orange crystals, mp 85–86 °C, 4.0 g (55%): IR ($CHCl_3$) ν_{CO} 1875 and 1825 cm^{-1}; NMR ($CDCl_3$) δ 1.50 (d, J_{HP} = 9 Hz, 6 H), 1.85 (s, 9 H), 4.35 (d, J_{HP} ~ 1 Hz, 3 H), 7.45 ppm (m, 5 H). Anal. Calcd for $C_{19}H_{23}CrO_2P$: C, 62.29; H, 6.33. Found: C, 62.66; H, 6.29. **7:** $(C_6H_6)Cr(CO)_3$ (1.1 g) and PPhBzMe (1.6 g) in 100 mL of benzene (Pyrex flask) were irradiated by an external lamp for 5 h. Chromatography (alumina, benzene:hexane, 2:8) and recrystallization (benzene:hexane) afforded 1.0 g (51%) of yellow crystals, mp 118–119 °C; IR ($CHCl_3$) ν_{CO} 1885, 1820 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (d, J_{HP} = 4 Hz, 3 H), 3.2 (m, 2 H), 4.65 (d, J_{HP} ~ 1.5 Hz, 3 H), 7.2–7.4 ppm (m, 10 H). Anal. Calcd for $C_{22}H_{21}CrO_2P$: C, 66.00; H, 5.29. Found: C, 65.90; H, 5.21. **8:** (mes)$Cr(CO)_3$ (0.47 g) and PPhBzMe (0.6 g) in 30 mL of benzene (Pyrex flask) were irradiated externally for 4 h. Chromatography (alumina, hexane:benzene, 7:1) and crystallization (hexane) afforded 230 mg of orange crystals (28%), mp 131–132 °C. Irradiation of the reactants in THF solvent gave none of the desired product: IR ($CHCl_3$) ν_{CO} 1865, 1805 cm^{-1}; NMR ($CDCl_3$) δ 1.38 (d, J_{HP} = 5 Hz, 3 H), 1.8 (s, 9 H), 3.2 (m, 2 H), 4.35 (d, J_{HP} ~ 1.5 Hz, 3 H), 6.6–7.2 ppm (m, 10 H). Anal. Calcd for $C_{25}H_{27}CrO_2P$: C, 67.86; H, 6.15. Found: C, 67.83; H, 6.08. **9:** (mes)$Mo(CO)_3$ (1.0 g) and PPhBzMe (1.0 g) in 300 mL of ether were irradiated in the immersion apparatus (Pyrex filter) for 5 h, while the apparatus was immersed in a salt water–ice bath. Chromatography (alumina, hexane then benzene) and crystallization (hexane:benzene) yielded orange crystals, 0.8 g (49%), mp 125–126 °C: IR ($CHCl_3$) ν_{CO} 1870, 1810 cm^{-1}; NMR ($CDCl_3$) δ 1.50 (d, J_{PH} = 7 Hz, 3 H), 2.0 (s, 9 H), 3.4 (m, 2 H), 4.60 (s, 3 H), 6.6–7.6 ppm (m, 10 H). Anal. Calcd for $C_{25}H_{27}MoO_2P$: C, 61.73; H, 5.60. Found: C, 61.77; H, 5.56.

Compounds **4, 5,** and **6** could not be prepared as above, because only arene displacement occurred for **4**, and only bis substitution by two phosphines occurred for compounds **5** and **6.** The following variation was therefore used. **4:** (mes)$W(CO)_3$ (0.7 g) was irradiated in 300 mL of THF in the immersion apparatus (Pyrex filter) for 6 h, resulting in a dark red solution (presumably (mes)$W(CO)_2$(THF)). $PPhMe_2$ (0.3 g) was added and the solution was stirred at 25 °C overnight. Otherwise, the procedure was as above. Chromatography (alumina, hexane:ethyl acetate, 98:2) and crystallization (hexane) yielded 60 mg (79%) of orange crystals, mp 115–116 °C: IR ($CHCl_3$) ν_{CO} 1870, 1810 cm^{-1}; NMR ($CDCl_3$) δ 1.88 (d, J_{HP} = 11 Hz, 6 H), 2.13 (s, 9 H), 4.52 (s, 3 H), and 7.43 ppm (m, 5 H). Anal. Calcd for $C_{19}H_{23}O_2PW$: C, 45.81; H, 4.65. Found: C, 45.81; H, 4.64. **5:** $CpMn(CO)_3$ (2.0 g) in 300 mL of THF was irradiated in the immersion apparatus (Pyrex filter) for 4 h, and then $PPhMe_2$ (2.8 g) was added to the orange solution. After 6 h at 25 °C, the reaction was worked up as usual. Chromatography (alumina, hexane:benzene, 1:1) and crystallization (hexane:benzene) afforded yellow crystals, 1.5 g (48%), mp 92–93 °C: IR ($CHCl_3$) ν_{CO} 1935, 1865 cm^{-1}; NMR ($CDCl_3$) δ 1.80 (d, J_{HP} = 8 Hz, 6 H), 4.44 (br s, 5 H), 7.5 ppm (m, 5 H). Anal. Calcd for $C_{15}H_{16}MnO_2P$: C, 57.33; H, 4.83. Found: C, 57.39; H, 5.00. **6:** $(C_5H_4(CH_3))Mn(CO)_3$ (4 g) in 200 mL of THF was irradiated in the immersion apparatus (Pyrex filter) for 20 h. Then $PPhMe_2$ (3.8 g) was added to the orange solution, and after standing overnight at 25 °C the reaction mixture was worked up in the usual way. Chromatography (alumina, hexane:benzene, 1:1) and crystallization from hexane yielded orange crystals, 1.2 g (20%), mp 60–61 °C: IR ($CHCl_3$) ν_{CO} 1925, 1855 cm^{-1}; NMR ($CDCl_3$) δ 1.66 (d, J_{HP} = 12 Hz, 6 H), 1.80 (s, 3 H), 4.26 (m, 4 H), 7.47 ppm (m, 5 H). Anal. Calcd for $C_{16}H_{18}MnO_2P$: C, 58.73; H, 5.24. Found: C, 58.25; H, 5.45.

CpMo(CO)$_2$(PPhBzMe)H (10). $(CpMo(CO)_3)_2Hg$[23] (2.1 g) and PBzPhMe (1.3 g) were heated at reflux in 150 mL of benzene overnight. The product was purified by chromatography (alumina, hexane-ethyl acetate, 8:2) to yield 2.45 g (96%) of yellow crystalline $[CpMo(CO)_2(PBzPhMe)]_2Hg$.[24] This product (1.2 g) in 50 mL of THF was reduced with 0.2 g of Na in 10 mL of Hg for 4 h and the anion was protonated with 1 mL of acetic acid.[27] Purification by chromatography (alumina, hexane, then hexane-benzene, 8:2) yielded a light yellow oil, 0.7 g: IR, $\nu_{C\equiv O}$ 1940, 1860 cm^{-1}; NMR, (C_6D_6) δ 1.46 (d, J_{HP} = 8 Hz, 3 H), 3.2 (m, 2 H), 4.65 (s, 5 H), and 7.2 (m, 10 H) ppm. Satisfactory combustion analyses could not be obtained because of the air sensitivity of the oil.

CpFe(CO)(PPhBzMe)H (11). CpFe(CO)(PBzPhMe)I was prepared by heating 3 g of $CpFe(CO)_2I$ and 2.4 g of PBzPhMe in 100 mL of xylene at reflux for 3 days. Chromatography (alumina, benzene) afforded 0.65 g of green crystalline product, mp 95–96 °C. Then 0.2 mL of a 70% solution of $NaAlH_2(OMe)(OEt)$ in benzene was added to 0.25 g of CpFe(CO)(PBzPhMe)I in 40 mL of benzene, and the solution was stirred at 25 °C for 3 h. The reaction mixture was hydrolyzed with 2 mL of water, the benzene layer was separated and dried (Na_2SO_4), and the solvent was evaporated. Chromatography of the residue (alumina, hexane, then hexane-benzene, 1:1) yielded a yellow oil, 70 mg (39%): IR, $\nu_{C\equiv O}$ 1925 cm^{-1}; NMR (C_6D_6), δ 1.38 (d, J_{HP} = 8 Hz, 3 H), 3.2 (m, 2 H), 4.32 (s, 5 H), 6.7–7.8 (m, 10 H) ppm. Anal. Calcd for $C_{20}H_{21}FeOP$: C, 65.95; H, 5.81. Found: C, 65.76; H, 5.84.

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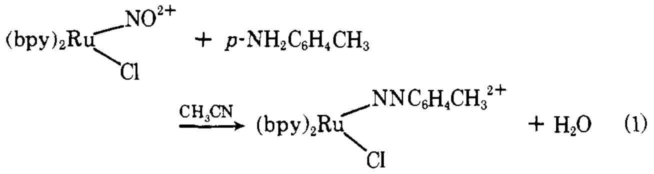
Diazotization of Aromatic Amines by Ruthenium Nitrosyl Complexes

William L. Bowden, William F. Little, and Thomas J. Meyer*

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514. *Received September 30, 1976*

Abstract: The ruthenium nitrosyl complex $[Ru(bpy)_2(NO)Cl]^{2+}$ (bpy is 2,2′-bipyridine) reacts with the aromatic amines p-$NH_2C_6H_4$-Y (-Y is $-OCH_3$, $-CH_3$, -H) in acetonitrile to give the corresponding diazonium complexes $[Ru(bpy)_2(N_2Ar)Cl]^{2+}$ which have been isolated and characterized as hexafluorophosphate salts. The properties of the complexes are consistent with a considerable degree of diazonium ion character in the Ru-NNAr linkage including broad, sometimes structured $\nu(NN)$ stretching frequencies at 1980–2100 cm^{-1}. The bound ligands undergo a series of reactions including an irreversible one-electron reduction, thermal reactions in water with I^- and acetone, and diazo coupling with β-naphthol. Qualitative infrared studies in the $\nu(NN)$-$\nu(NO)$ stretching frequency region show that the rates of the diazotization reactions are sensitive to the natures of the nitrosyl complex and the amine, and that a series of stepwise reactions is probably involved in the overall reactions.

In an earlier communication we described preparations for a series of aryldiazo complexes[1] which were obtained as products of reactions between ruthenium nitrosyl complexes and aromatic amines, e.g., eq 1.[2] Both the chemistry involved in the net reactions (eq 1) and the electronic structure of the products have features of importance for chemical problems of a more general nature.



$$(bpy)_2Ru\begin{matrix}NO^{2+}\\ Cl\end{matrix} + p\text{-}NH_2C_6H_4CH_3 \xrightarrow{CH_3CN} (bpy)_2Ru\begin{matrix}NNC_6H_4CH_3^{2+}\\ Cl\end{matrix} + H_2O \qquad (1)$$

A series of reports has shown that the nitrosyl groups in complexes of the type $[Ru(bpy)_2(NO)L]^{n+}$ (n = 2, Br, N_3, NO_2; n = 3, H_2O, NH_3, py, CH_3CN) behave chemically much as does the nitrosonium ion (NO^+). As examples the bound NO group has been found to react with the nucleophiles OH^- [3] and N_3^-,[4] to add as an electrophile to activated aromatics,[5] and to undergo reversible one-electron reduction.[6] The unusual reactivity of the bpy ions when compared with other metal nitrosyls can be attributed to a considerable degree of NO^+ character in the formally $(d^6)Ru(II)-NO^+$ linkage which arises because of the relatively high formal oxidation state at the metal, the positive charge on the complexes, and competitive back-bonding with the 2,2′-bipyridine ligands.[6] The relatively high $\nu(NO)$ stretching frequencies for the complexes are consistent with this view,[7] as are the variations in $\nu(NO)$ as the group cis to NO is varied in the series N_3, Cl, NO_2, NH_3, py, and CH_3CN.[6] The NO group in the complexes can effectively be taken as a chemically modified form of the nitrosonium ion. The nitrosyl complexes, which are conveniently prepared under usual nitrosating conditions,

$$[Ru(bpy)_2(H_2O)Cl]^+ + NO_2^- \xrightarrow{H^+} [Ru(bpy)_2(NO)Cl]^{2+}$$ [3]

then represent reagents in which a useful but reactive inter-