(6) Other ylide complexes have been found to be useful for ethylene polymerization catalysts: U.S. Patents 2 998 416 (1961) and 3 686 159 (1972).

(7) All proton chemical shifts are reported with respect to Me_4Si.

(8) Due to the low solubility of **1** in any nonreactive solvent, a pulsed NMR technique was necessary to obtain this spectrum. The authors wish to thank Dr. George Gray of Varian Associates for obtaining this spectrum.

(9) The ^{31}P chemical shifts are downfield with respect to external 85% H_3PO_4.

(10) The details of these variable temperature ^1H NMR studies will be reported elsewhere.

(11) Hydroformylations of ethylene, 1-hexene, and butadiene were attempted in benzene solution at 100 °C and pressures of CO/H_2 (1:1) up to 1200 psi. At temperatures of 150 °C and above hydroformylation did occur, but at these temperatures the catalyst decomposed to give rhodium metal.

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Natural Abundance Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy of Some Rhodium(III) Complexes

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The natural abundance nitrogen-15 NMR spectra of the rhodium(III) complexes of several alkyldiamine and aza aromatic ligands are reported. Spectra were obtained in several hours for the first class of compounds but required ca. 15 h for the latter group. Spectra could not be observed for a number of other complexes. The resonances of the complexes are found ca. 20 ppm upfield from those of the free ligand in the alkyldiamine case but are ca. 100 ppm above the aza aromatic ligands. This is attributed to shifts arising from the influence of low-lying excited states for the aza aromatic ligands themselves rather than any special property of their complexes. When comparison is made between the chemical shift of the complex and that of the protonated ligand, a rather constant difference of ca. 30 ppm is observed. No correlation of shift with position of the ligands in the spectrochemical series is observed. It is suggested that the upfield shift generally observed is a consequence of nonbonded magnetic interactions. Coupling constants between nitrogen-15 and rhodium-103 are observed and correlate simply with the s character of the bonding electron on nitrogen with $J = 18$ Hz for sp^2 and $J = 14$ Hz for sp^3. Diastereoisomerism is detectable in the tris complex of 1,2-diaminopropane, and rather rigid, different ligand conformations are observed for the tris(1,3-diaminopropane) case.

Introduction

The nuclear magnetic resonance spectroscopy of nitrogen in coordination compounds is an area of considerable potential interest. Nitrogen is a constituent of many ligands which are important in coordination chemistry and biochemistry. Furthermore, unlike carbon and hydrogen, nitrogen is often bound directly to the metal ion, and its spectroscopy can be expected to be a sensitive probe of bonding, coordination geometry, electronic structure, etc. Nitrogen exists in nature as two isotopes. The most abundant one, ^{14}N, has $S = 1$, and so its resonances are often quite broad in nonzero electric field gradients. In some situations this is not a problem, and its spectroscopy has yielded important information.[1] ^{15}N, however, has $S = {}^1/_2$ and so its resonances should be sharp and should reveal spin coupling when present. This isotope, unfortunately, is characterized by a rather low abundance (0.365%) and long relaxation times. These problems have largely restricted its natural abundance study to organic molecules which are liquids or are very soluble. A few studies have been performed with organometallic or coordination compounds, but these have been restricted to ligands enriched in ^{15}N. For example, the chemical shifts of coordinated ammonia have been measured via an ENDOR method,[2] and the mode of bonding was identified in a dinitrogen complex.[3] The most thorough study of ^{15}N shifts in coordination compounds has been the work carried out using ^{15}N-enriched ethylenediaminetetraacetate (EDTA) and a series of closed-shell metal ions. In this study it was demonstrated that shifts of only a few parts per million are observed when EDTA binds such closed-shell metal ions as Ca^{2+}, Zn^{2+}, Mg^{2+}, etc. This disappointingly small shift was attributed to near cancellation of large local diamagnetic and paramagnetic effects at the nitrogen atom.

Herein we report the natural abundance nitrogen-15 spectroscopy of a series of rhodium(III) complexes. This metal ion was chosen for a variety of reasons. Its complexes are always diamagnetic and substitutionally inert, excluding ground-state paramagnetic or ligand-exchange effects from consideration. As a d^6 ion, however, it has fairly low-lying excited states whose admixture might lead to large chemical shifts and whose energies are readily varied by utilizing ligands from different parts of the spectrochemical series. Also, it exists entirely as ^{103}Rh with $S = {}^1/_2$, and so one can obtain coupling constant data.

Experimental Section

Abbreviations of ligands appear in footnote 5. The rhodium(III) compounds $Rh(en)_3Cl_3$, $Rh(pn)_3Cl_3$, and $Rh(tn)_3Cl_3$ were prepared by the method of Gatsbol[6] while $Rh(bpy)_3Cl_3$ and $Rh(phen)_3\,Cl_3$ were prepared by the method of McKenzie and Plowman.[7] $Rh(en)_2Cl_2Cl$ and $Rh(py)_4Cl_2Cl$ were prepared by the methods of Anderson and Basolo[8] and of Gillard and Wilkinson,[9] respectively.

The ^{15}N NMR spectra were obtained in Fourier Transform mode with JEOL PS/PFT-100 spectrometer interfaced to a JEOL EC-100 data system. Chemical shifts at 10.09 MHz were determined using a 5 kHz range and 8K memory and are measured with respect to an external ammonium chloride solution. In the case of aliphatic amine complexes, a pulse angle of about 60° and in the case of aza aromatic complexes, a pulse angle of about 25–30° was used. For all complexes H_2O was the solvent, except in the case of the pyridine complex which was dissolved in benzyl alcohol. The spectra of the bis(ethylenediamine) and tetrakis(pyridine) complexes were obtained at 50 °C to have sufficient concentration.

Results and Discussion

Table I presents the chemical shift data obtained from the present studies. It also indicates the experimental conditions necessary to obtain these spectra. The most favorable cases are those of the bidentate saturated amines, which have protonated nitrogen atoms. Spectra are easily obtained within 2–4 h at concentrations of 1–2 M. Figure 1 is the spectrum

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Table I. Nitrogen-15 Chemical Shifts of Ligands and Their Rhodium(III) Complexes and Rh–N Coupling Constants[a]

Complex	Protonated ligand, ppm	Free ligand, ppm	Coordinated ligand, ppm	$J_{\text{Rh–N}}$, Hz	Scans[f]
$Rh(en)_3Cl_3$	8.6	−6.5[c]	−31.8	14.6	800
$Rh(pn)_3Cl_3$	21.7	9.8[c]	−15.5	(13.5)[g]	29 000
	7.7	−9.4	−34.5		
$Rh(tn)_3Cl_3$	10.3	−1.7[c]	−44	(14.3)[g]	30 000
$Rh(bpy)_3Cl_3$	195.4	280.7[c]	186.1	18.1	10 000
$Rh(phen)_3Cl_3$	211.4	273.1[d]	180.8	18.4	25 000
(*trans*-$Rh(en)_2Cl_2$)Cl	8.6	−6.5[c]	−28.6	13.4	5 000
(*trans*-$Rh(py)_4Cl_2$)Cl	176.9	289.6[c]	191[e]	17.1	46 000
(*cis*-$Rh(bpy)_2Cl_2$)Cl		No spectrum observed			50 000
(*cis*-$Rh(phen)_2Cl_2$)Cl		No spectrum observed			50 000
$Rh(py)_3(SCN)_3$		No spectrum observed			50 000
$Rh(CH_3CN)_3Cl_3$		No spectrum observed			50 000

[a] Shifts are downfield from an internal capillary of $^{15}NH_4Cl$. [b] In H_2O–HCl. [c] In $CDCl_3$. [d] In CH_3OD. [e] At 50 °C. [f] Number of scans to obtain at least 10:1 signal to noise for 2 M or saturated solution. [g] Average coupling constants for the isomers present.

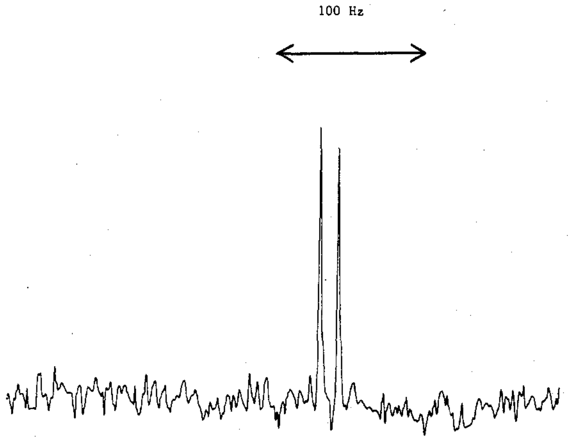

Figure 1. ^{15}N spectrum of $Rh(en)_3Cl_3$ at 10.09 MHz: 1.5 M solution in H_2O; 800 scans with a pulse angle of ca. 60°.

obtained for the tris(ethylenediamine) complex. The aromatic heterocyclic amines, however, lack directly bonded protons, and obtaining the spectra of their complexes is significantly more difficult. Here spectra could only be obtained for the most symmetrical complexes and then only with accumulations of 10 000 or more scans. Table I also lists a number of cases where no spectra could be obtained. All these complexes lack protons on the nitrogens and their symmetries are low.

The relatively short times required to obtain spectra of complexes whose nitrogen atoms have directly bonded hydrogen is probably the result of signal enhancement due to the nuclear Overhauser effect resulting from proton noise decoupling plus the shorter relaxation times enjoyed by such nitrogen atoms. Paramagnetic relaxation reagents have been used to shorten relaxation times in carbon-13 spectroscopy; however, the addition of tris(ethylenediamine)chromium(III) chloride did not help in cases where no spectra had been obtained.

Chemical Shifts. In Table I, a comparison is made among the chemical shifts of the complexes, the free ligands, and the protonated ligands. Chemical shifts are interpreted by means of the Ramsey equation, which treats the observed shielding as a combination of three terms as in eq 1[10]. The σ_p term

$$\sigma = \sigma_p + \sigma_d + \sigma_1 \qquad (1)$$

is the paramagnetic component and consists of a summation of terms whose numerators are matrix elements between ground and excited states and whose denominator is the difference in energy between the ground and excited state. It is a number of negative sign and results in shifts in the downfield direction. The σ_d term is the diamagnetic component arising from the electron density around the atom in question in its ground state and is in the upfield direction. The σ_1 term is a term arising from the effects of neighboring atoms. This term is often ignored; however, in cases where the nucleus in question is next to a transition metal, the term can be rather large. In the transition-metal hydrides, upfield shifts of 20–30 ppm are observed for the hydride and are the result of the σ_1 term.[11]

Table II. Chemical Shift on Replacement of a Proton by Rhodium(III)

Protonated ligand	δ, ppm	Complex	δ, ppm	Diff, ppm
enH_2^{2+}	8.6	$Rh(en)_3Cl_3$	−31.8	−40.4
		$(Rh(en)_2Cl_2)Cl$	−28.6	−37.2
pnH_2^{2+}	21.7	$Rh(pn)_3Cl_3$	−15.5	−37.2
	7.7		−34.5	−42.2
tnH_2^{2+}	10.3	$Rh(tn)_3Cl_3$	−44	−54.3
$phenH^+$	211.9	$Rh(phen)_3Cl_3$	180.8	−30.6
$bpyH^+$	195.4	$Rh(bpy)_3Cl_3$	186.6	−9
pyH^+	176.9	$(Rh(py)_4Cl_2)Cl$	191.0	+14.1

In Table I, an upfield shift is observed when the free ligands coordinate rhodium(III). In the cases of the saturated ligands, the shift is 25 to 42 ppm; however, the shift is approximately 100 ppm for the aromatic ligands. Table I also contains the chemical shifts of the protonated ligands. Inspection shows that the different behaviors of aliphatic and aromatic ligands on coordination are similar to their different behaviors upon protonation. A brief digression on the effects of protonation is therefore instructive.

Table I shows that for the saturated ligands there is a 10–15 ppm downfield shift when the free base is protonated, whereas shifts as much as 100 ppm upfield are noted when the aromatic ligands are protonated. These observations are consistent with results obtained for ^{15}N shifts in analogous systems. For aliphatic amines, the downfield shift upon protonation has been attributed to changes in the σ_d term of eq 1. Thus, protonation is thought to cause a downfield shift mainly by withdrawing electron density and decreasing the diamagnetic component of shielding.[12] For aromatic amines, the free ligand is found to lower field than the protonated ligand. Here, it is believed that the paramagnetic term is primarily responsible. The excitation energy for the lone pair of electrons on the nitrogen of the free base is much lower than when this pair binds a proton. Hence a much larger paramagnetic term is anticipated for the free base than for the protonated ligand.[13]

Thus, the difference between the behavior of aromatic and aliphatic ligands upon protonation has been traced to the low excitation energy of the aromatic free base lone pair. Lone-pair effects in the comparison of ligands to complexes may be eliminated from consideration by instead compairing protonated ligands to the metal complex. Table II makes such a comparison. It shows that rather similar upfield shifts are observed for both aromatic and aliphatic ligands when rhodium(III) replaces a proton.

Roberts and co-workers have studied the ^{15}N resonances of a large group of closed-shell metal complexes of EDTA.[4] Shifts of less than 20 ppm were observed for all complexes. Utilizing an approximate formula suggested for the calculation of diamagnetic shielding in small molecules, these authors assumed neglible polarity of the metal–ligand bond and calculated values of σ_d which are large and increase sharply with the atomic number of the metal. To rationalize the relatively small shifts observed, they postulated that a large paramagnetic term must also arise from coordination and that its magnitude must nearly equal the diamagnetic term, almost canceling it. Since the metal ion is the same in all the cases we report, its contribution to the diamagnetic term should be fairly constant from complex to complex. The metal ion's contribution to σ_p could be large because it has an unfilled shell and low-lying excited states. If such a σ_p term were large, one would expect to observe chemical shifts which are strongly dependent on the type of ligand because the energies of the excited states are determined by the position of the ligands in the spectrochemical series. Since the σ_p term has the excitation energy in its denominator, one would expect an inverse relationship between σ_p and the average position of the ligands in the spectrochemical series. If for a series of complexes σ_p is large and σ_d is constant, the observed shielding should correlate with the spectrochemical series.[14] No such correlation can be made from the data in Table I. The tris(1,3-diaminopropane) (tn) complex, for example, is found to higher field than the en complex. However, for the corresponding cobalt(III) complexes, tn is lower in the spectrochemical series and its complex has the longer wavelength absorption. Also, *trans*-dichlorobis(ethylenediamine)rhodium(III) falls only 3 ppm to lower field than the tris(ethylenediamine) complex, despite the much lower position of chloride in the spectrochemical series.

It appears that the σ_p term for the effect of the metal ion on the ligand nitrogen atom is not large in the complexes we have studied. Since the shifts observed on coordination are small, σ_d must also be in the range of 10–30 ppm, as opposed to the values greater than 100 ppm suggested by Roberts. The smaller values are more in keeping with the 10-ppm shift observed when saturated amines are protonated.

The changes in σ_p and σ_d at nitrogen are evidently small when a proton is replaced by a rhodium(III) ion. It remains to suggest a plausible explanation for the relatively large and constant upfield shift observed upon coordination in Table II. A simple explanation would lie in σ_1 of eq 1. It seems likely that these upfield shifts are similar to those observed in proton spectroscopy when a transition-metal hydride is formed. Here it has been shown that the d orbitals of the metal ion interact with the magnetic field to shield the attached proton.[11] Thus, the model we suggest is one where the nitrogen nucleus is not affected much by coordination to a metal ion except that it finds itself adjacent to a magnetically active neighbor which makes a rather large contribution to σ_1. Long-range shielding of this type depends inversely on the excitation energy. It also depends inversely on the cube of the internuclear separation. The effect should parallel the spectrochemical series if the metal–nitrogen bond lengths were constant. The complexes we have studied differ substantially from one another. Bond lengths vary considerably, and this is magnified when they are cubed. Therefore, it is unwise to make a more quantitative comparison among the complexes in order to evaluate σ_1. This will require the study of a much more closely related series of compounds.

Coupling Constants. The coupling constants are easily rationalized in terms of the metal–nitrogen bonding. Table I shows that saturated nitrogens couple to ^{103}Rh with J = 13–14 Hz, while the aromatic nitrogens couple with J = 18 Hz. The ratio of these values is nearly exactly that of the ratio of s character in pure sp^3 and sp^2 hybrids. Equation 2 is the

$$^1J_{^{103}\mathrm{Rh}-^{15}\mathrm{N}} = \frac{(\alpha_{\mathrm{Rh}})^2(\alpha_{\mathrm{N}})^2[\psi_{\mathrm{Rh}5s}(0)]^2[\psi_{\mathrm{N}2s}(0)]^2}{\Delta E} \qquad (2)$$

theoretical expression for nuclear spin coupling, where ΔE is the singlet–triplet excitation energy, the α's are the s character of the hybrids at each atom, and the $\psi(0)$'s are the electron densities at the respective nuclei. It is noteworthy that this metal ion excitation energy does not vary enough to influence the simple ratio of coupling constant to hybridization. Similar observations have been made in studies of the coupling between platinum-195 and directly bonded nuclei. In platinum phosphines, the magnitude of $J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ is independent of excitation energy and determined mainly by the bonding of the complex.[16] Likewise, ^{13}C–^{195}Pt couplings are governed by hybridization of the carbon atom[17] and ^{15}N–^{195}Pt couplings are dependent on the ratio of s character between the hybridization of the platinum in octahedral and square-planar complexes.[18]

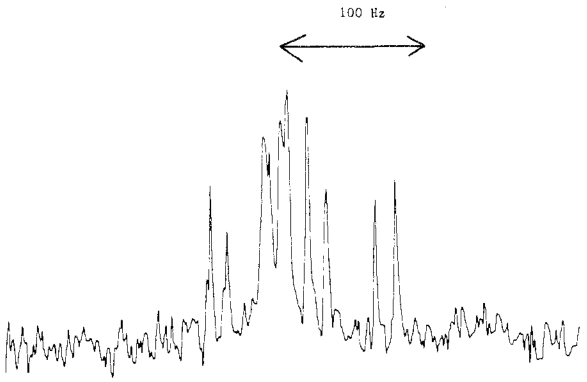

Figure 2. ^{15}N spectrum of $Rh(tn)_3Cl_3$ at 10.09 MHz: 2 M solution in H_2O; 30 000 scans with a pulse angle of ca. 60°.

Chemical Effects. Spectra were usually unobservable under our conditions for complexes with nonequivalent nitrogen atoms. The saturated amines were the only exceptions. Ethylenediamine chelate rings are nonplanar, leading to nonequivalence of the nitrogen donors; however, separate resonances are not observed, no doubt because of the rapid intraconversion of isomers. For 1,2-propylenediamine complexes, diastereoisomers are expected for the tris complex. These were observed, but the chemical shifts between isomers are small, on the order of only 2–3 Hz. For 1,3-propylenediamine, the coordinated ligand may have boat, chair, and skew-boat conformations. The tris cobalt(III) complex has equivalent ligands in the solid state,[19] though an equilibrium may exist with skew-boat forms in solution.[20] The somewhat larger chromium(III) has two equivalent tn ligands in chair forms facing one another and a third one in skew-boat conformation.[21] Equilibrium among the ligands is expected to be rapid. Figure 2 shows the ^{15}N spectrum of the (tn)–Rh^{III} complex. Though the structure of the complex cannot be inferred, it is clear not only that the ligands are nonequivalent but also that they intraconvert slowly on the NMR time scale. The carbon-13 spectrum shows the same multiplicity. By contrast, the ^{13}C spectrum of the corresponding cobalt(III) complex is simply two singlets, one for each of the different carbon atoms.

Conclusions

Natural abundance ^{15}N spectra may be obtained for rhodium(III) complexes if the nitrogens have directly bonded protons. If the ligands do not have directly bonded protons, spectra are obtainable for large ligands in relatively symmetrical environments. The chemical shifts are not large and are usually to high field. No simple rationalization of the shifts can be made; however, the constancy of values observed suggests that they are largely due to nonbonded effects. Coupling constants appear to be sharply dependent on the hybridization of the nitrogen and may afford a convenient measure of the s character of metal–nitrogen bonds.

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Registry No. $Rh(en)_3Cl_3$, 14023-02-0; $Rh(pn)_3Cl_3$, 14175-72-5; $Rh(tn)_3Cl_3$, 64175-36-6; $Rh(bpy)_3Cl_3$, 32680-72-1; $Rh(phen)_3Cl_3$, 27353-21-5; (*trans*-$Rh(en)_2Cl_2$)Cl, 15444-63-0; (*trans*-$Rh(py)_4Cl_2$)Cl, 14077-30-6; enH_2^{2+}, 22534-20-9; pnH_2^{2+}, 62063-19-8; tnH_2^{2+}, 61696-59-1; $phenH^+$, 22559-75-7; $bpyH^+$, 20755-72-0; pyH^+, 16969-45-2; en, 107-15-3; pn, 78-90-0; tn, 109-76-2; bpy, 366-18-7; phen, 66-71-7; py, 110-86-1; ^{15}N, 14390-96-6.

References and Notes

(1) N. Logan in "Nitrogen NMR", M. Witanowski and G. A. Webb, Ed., Plenum Press, New York, N.Y., 1973.

(2) J. W. Lehman and B. M. Fung, *Inorg. Chem.*, **11**, 214 (1972).

(3) J. E. Bercaw, E. Rosenberg and J. D. Roberts, *J. Am. Chem. Soc.*, **96**, 612 (1974).

(4) R. Hagen, J. P. Warren, D. H. Hunter, and J. D. Roberts, *J. Am. Chem. Soc.*, **95**, 5712 (1973).

(5) The abreviations used are: en = ethylenediamine; pn = 1,2-diaminopropane; tn = 1,3-diaminopropane; bpy = 2,2-bipyridine; phen = 1,10-phenanthroline; py = pyridine.

(6) F. Gatsbol, *Inorg. Synth.*, **12**, 269 (1970).

(7) E. D. McKenzie and R. A. Plowman, *J. Inorg. Nucl. Chem.*, **32**, 199 (1970).

(8) S. N. Anderson and F. Basolo, *Inorg. Synth.*, **7**, 214 (1963).

(9) R. D. Gillard and G. Wilkinson, *Inorg. Synth.*, **10**, 64 (1967).

(10) N. F. Ramsey, *Phys. Rev.*, **91**, 903 (1953).

(11) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747 (1964).

(12) (a) J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **51**, 735 (1964); (b) W. M. Lichtman, M. Alei, Jr., and A. E. Florin, *J. Am. Chem. Soc.*, **82**, 6574 (1960).

(13) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **8**, 19 (1964).

(14) R. Freeman, G. R. Murray, and R. E. Richards, *Proc. R. Soc. London, Ser. A*, **242**, 455 (1957).

(15) R. Bramely, B. N. Figgis, and R. S. Nyholm, *J. Chem. Soc. A*, 861 (1967).

(16) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(17) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).

(18) P. S. Pregosin, H. Omura, and L. M. Venanzi, *J. Am. Chem. Soc.*, **95**, 2047 (1973).

(19) T. Noumura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 1016 (1969).

(20) P. G. Beddoe, M. J. Harding, S. F. Mason, and B. J. Peart, *Chem. Commun.*, 1283 (1971).

(21) F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, **13**, 2387 (1974).

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Metalation of Acetyl- and Dimethylaminomethylferrocenes with Pentacarbonyl(methyl)manganese or -rhenium: Formation of Homoannular Metalated Ferrocenes and Ferrocenylmethylaminomethylene(tetracarbonyl)manganese[1,2]

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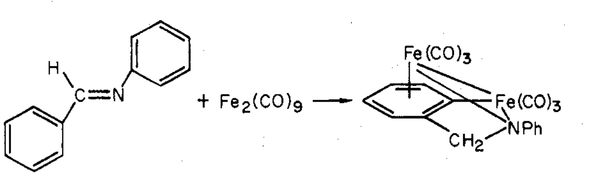
The homoannular metalation products tetracarbonyl(2-acetylferrocenyl)manganese (**3**) and -rhenium (**2**) and tetracarbonyl(2-dimethylaminomethylferrocenyl)rhenium (**9**) have been isolated and characterized. The cyclometalated product **3** is found to be much more labile to reaction with donor molecules than the phenyl analogue, tetracarbonyl(2-acetylphenyl)manganese. While **3** readily reacts with CO to form pentacarbonyl(2-acetylferrocenyl)manganese (**4**) the phenyl compound fails to show any reaction even at elevated temperature. While both species react with triphenylphosphine to form the phosphine-substituted facial tricarbonyl (e.g., *fac*-tricarbonyl(triphenylphosphino)-2-acetylferrocenylmanganese), **5**, the phosphine substitution occurs more rapidly for the ferrocenyl analogue. Treatment of benzoylferrocene with pentacarbonyl(methyl)manganese leads solely to metalation on the phenyl ring giving tetracarbonyl(2-ferrocenylcarbonylphenyl)manganese (**7**). The cyclometalated ferrocenylamine **9** undergoes electron oxidation with $FeCl_3$. Cyclic voltammetry indicates a reversible oxidation at +0.17 V (vs. SCE), lowered from that in the free amine (+0.43 V vs. SCE). The reaction of pentacarbonyl(methyl)manganese with dimethylaminomethylferrocene leads to a cyclometalation product involving the methyl group on nitrogen, i.e., tetracarbonyl(*N*-ferrocenylmethyl-*N*-methylaminomethylene)manganese (**10**).

Introduction

Up to the present study, the great majority of aromatic metalation reactions by transition metals have been observed for functionalized phenyl rings.[3] The present work was initiated to explore the metalation of substituted metallocenes, of which only a limited number of examples can be cited. It was earlier reported that FcCH=NPh [Fc = ferrocenyl, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{–})$] failed to undergo metalation by $Fe_2(CO)_9$ analogous to that observed for PhCH=NPh (eq 1).[4]



(1)

As suggested by these authors, the negative result for the metallocene is most likely due to the unavailability of the cyclopentadienyl ring π electrons for interaction with the second iron tricarbonyl moiety, a feature required in metalation by $Fe_2(CO)_9$ of the Schiff base.

That metallocene or metal–π-bonded arene rings can be σ metalated by transition-metal complexes has since been demonstrated by report of a variety of complexes, I–V,[5,6] while Seiwell[6f] has postulated metalated intermediates in the catalyzed H/D exchange in ferrocene and in cyclopentadienylrhodium compounds.

During the study described here and independently of it, Alper[7a] has reported the metalation of thiopivaloylferrocene with Na_2PdCl_4 giving product VI. More recently, Gaunt and Shaw[7b] have observed cyclometalation of dimethylaminomethylferrocene by $PdCl_4^{2-}$. It should be noted as well that lithiation, and to a lesser extent sodiation, of substituted ferrocenes has been extensively studied.[8] Through such metalated derivatives, transition-metal substituents may be brought in via the usual metathetical reactions; the mono- and bis[tris(η^5-cyclopentadienyl)uranium]ferrocenes[9] may be cited as examples of syntheses using such a pathway.