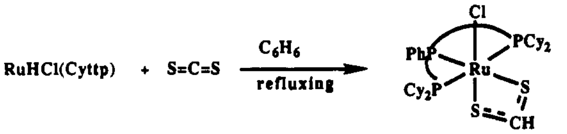
complex of ttp or Cyttp, the central and terminal phosphorus atoms could have very similar chemical shifts. In fact, the ^{31}P NMR spectrum for **4B** is very similar to that of *fac*-$Ru(O_2CMe)_2(ttp)$.[26] In structure **4B**, the coupling between the hydride and the two terminal phosphorus atoms could be similar in magnitude to that between the hydride and the central phosphorus atom, since P–H coupling constants are angular dependent[27] and cis,trans P–H coupling constants usually have opposite signs in metal complexes.[28]

The structure of **4C** is unclear on the basis of the spectroscopic data. The ^1H NMR spectrum shows no hydride resonance. In the aromatic region, besides the signal associated with the triphosphine ligand, there is a singlet at 6.08 ppm, corresponding to two protons per Cyttp on the basis of integration. The integration and absence of a hydride resonance suggest that **4C** might be $Ru(S_2CH)_2(Cyttp)$. The formation of $Ru(S_2CH)_2(PR_3)_3$ (PR_3 = PPh_2Me, $PPhMe_2$) from the reactions of CS_2 with $RuH_2(PR_3)_4$ is known. However, the value 6.08 ppm is too low for the chemical shift value for coordinated dithioformate protons (usually in the range 9.5–14 ppm).[9,10,23] This formulation is also inconsistent with the analytical data. The formulation of the compound as $Ru(S_2CH_2)(Cyttp)$ (structure **4C**) seems plausible. This formulation is consistent with analytical data and ^1H NMR integration. The signal at 6.08 ppm could be assigned to the S_2CH_2 protons. The value of 6.08 ppm is comparable with 6.25 ppm for the italic proton in S_2C*H*$-PMe_2Ph$ in the compound $[Ru(S_2CHPMe_2Ph)(PMe_2Ph)_3]PF_6$.[13] It has also been reported that the signals for bridged S_2CH_2 were observed at 6.31 ppm for $(CpMo)_2(S_2CH_2)(S_2CHCO_2Me)_2$ and 5.41 ppm for $(CpMo)_2(S_2CH_2)(S_2CH_2CO_2Me)_2$ in their ^1H NMR spectra.[29]

In contrast to $RuH_2(H_2)(Cyttp)$, the monohydride complex RuHCl(Cyttp) failed to react with CO_2, RN=C=NR (R = *p*-Tol, Cy). However, RuHCl(Cyttp) reacts with CS_2 smoothly in refluxing benzene to give $RuCl(S_2CH)(Cyttp)$ (**5**) (eq 2). The ^{31}P NMR spectrum of $RuCl(S_2CH)(Cyttp)$ shows a doublet at 4.4 ppm for the two terminal phosphorus atoms and a triplet at 15.4 ppm for the central phosphorus atom. In the ^1H NMR spectrum, the resonance for the dithioformate proton was observed at 11.45 ppm (dt, $^3J(PH)$ = 5.4, 3.4 Hz). Thus both the ^{31}P and ^1H NMR data are consistent with the triphosphine being meridional around ruthenium. In the infrared spectrum, the bands assignable to the coordinated dithioformate were observed at 1210 and 910 cm^{-1}. The dithioformate group in $RuCl(S_2CH)(Cyttp)$ is probably bidentate, to give an 18-electron complex.



(2)

Both $RuH_2(H_2)(Cyttp)$ and RuHCl(Cyttp) are reactive toward RNCS (R = Me, Ph, *p*-Tol). The products usually are mixtures and are soluble in common organic solvents. Thus it is difficult to separate and isolate pure compounds. The compounds formed in these reactions are most likely insertion products. Insertions of isothiocyanate into Ru–H bonds have been reported previously.[16]

Discussion

It was reported previously that $RuH_2(L)(PPh_3)_3$ (L = H_2, N_2, PPh_3)[7,8] reacted with CO_2 to give insertion product $RuH(O_2CH)(PPh_3)_3$, while $RuH_2(L)_4$ (L = PPh_2H, PPh_2Me, $PPhMe_2$)[8b] failed to react with CO_2. The failure was attributed to the unavailability of an unsaturated intermediate from dissociation of phosphines. This study shows that $RuH_2(H_2)(Cyttp)$ is more reactive than the 16-electron monohydride complex RuHCl(Cyttp) toward CO_2-like molecules. Thus the electronic property of an unsaturated metal center is also important to initiate CO_2 insertion.

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Hydrazinophosphine Complexes of Iron: Metallacycle Formation via Attack on Coordinated Carbon Monoxide

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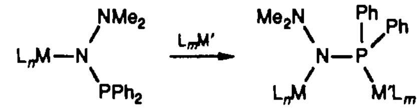
The polyfunctional ligand $Me_2NN(PPh_2)Li$ (**1**) has numerous possible coordination modes—amino, amido, and phosphino—which are capable of bonding in a monohapto fashion individually or in combination to produce chelated or bridged complexes. This variability in the nature of coordination, i.e., in both type and degree, makes these compounds attractive frameworks for the preparation of catalytically active compounds containing transition metals with complementary properties, such as early and late transition metals. Complexes of this type are of interest in catalytic reactions involving unsymmetric substrates such as the reduction of carbon monoxide.[2]

Initial investigations were designed to prepare hydrazinophosphine complexes of a single metal center such that the sole attachment of the ligand to the metal is a metal–nitrogen σ bond, thus leaving the phosphino fragment pendent (eq 1). Species of this type could then be used to prepare heterobimetallic compounds via coordination of a different metal to the phosphine.



(1)

The cyclopentadienyliron dicarbonyl fragment (Fp) was our first choice, due to its robust nature that would hopefully allow us to avoid oligomer formation via phosphine coordination by displacement of CO from other molecules of the complex.[3] Reaction of FpI with 1 equiv of **1** in THF at −80 °C produced a deep red solution that turns yellow-orange upon warming to room temperature. Removal of the volatile material from the reaction followed by extraction with methylene chloride and subsequent recrystallization from methylene chloride/ether yielded an orange crystalline material, **2**, in ca. 60% yield. Compound **2** displays a single resonance in the $^{31}P\{^1H\}$ NMR at δ 116 (relative to external H_3PO_4) indicating that the phosphorous is coordinated.[4]

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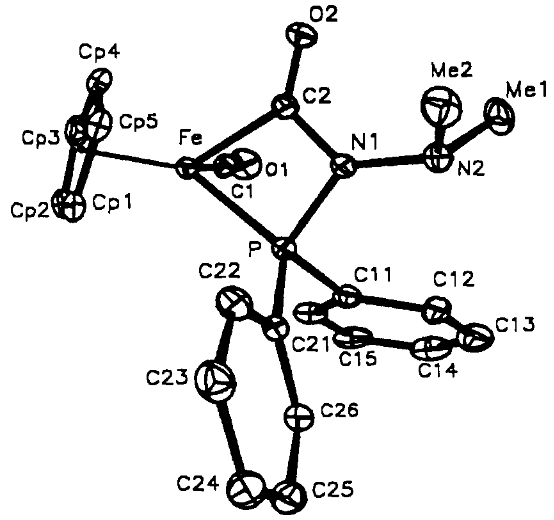


Figure 1. ORTEP view of **2** with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Fe–C(1), 1.717 (5); Fe–P, 2.182 (3); C(2)–N(1), 1.411 (5); N(1)–P, 1.697 (4); Fe–C(2)–N(1), 102.6 (3); Fe–P–N(1), 85.8 (1); P–Fe–C(2), 70.5 (1); C(2)–N(1)–P, 100.9 (3).

Additionally, there is a carbonyl stretch at low wavenumber, 1642 cm^{-1}. In light of these spectroscopic observations, an X-ray diffraction study was undertaken.

An ORTEP[5] diagram of **2** is shown in Figure 1. The product of the reaction is one in which a coordinated carbonyl has apparently inserted into a Fe–N bond formed by attack of the hydrazidophosphine on the metal center; however, since **2** is formed via the deprotonation of the coordinatively saturated phosphine complex [CpFe(CP)$_2$Me$_2$NN(PPh$_2$)][Cl] (vide infra), initial attack on coordinated CO is suggested. CO insertion into metal–carbon bonds is well-known while the corresponding insertion into metal–nitrogen bonds is relatively rare.[6]

The structure consists of a planar Fe–C–N–P metallacycle. The plane of the Cp ring is perpendicular to the metallacyclic plane. The only atoms that are not coplanar with the metal are the ancillary groups on the iron, the Cp ring and terminal CO, and the methyl and phenyl substituents on nitrogen and phosphorous, respectively. It is not immediately obvious if this situation results from electronic effects or is simply the most favorable arrangement in order to minimize the steric interactions of the ancillary groups with the atoms in the metallacycle.

Attempts were made to force the phosphino group of the hydrazidophosphine into a pendent position by displacement with a more nucleophilic phosphine, e.g. PMe$_3$, but no substitution was observed. The metallacyclic compound will react with electrophilic reagents. Treatment of a CH$_2$Cl$_2$ solution of **2** with anhydrous hydrogen chloride produces the cationic compound **3**, which formally has the protonated form of compound **1** coordinated via the phosphorous. Compound **3** was characterized spectroscopically by a change in the ^{31}P{^{1}H} NMR resonance to δ 106 (relative to external H$_3$PO$_4$) and the appearance of an N–H resonance in the ^{1}H NMR at δ 6.7, $^2J_{PH}$ = 22 Hz. A ORTEP diagram of the cation of **3** is shown in Figure 2.[7] The protonation is associated with a concomitant deinsertion of the ring carbonyl (eq 2). The observed reactivity of **2** with HCl is completely reversible. Treatment of **3** with 1 equiv of butyllithium produces **2** quantitatively by NMR.

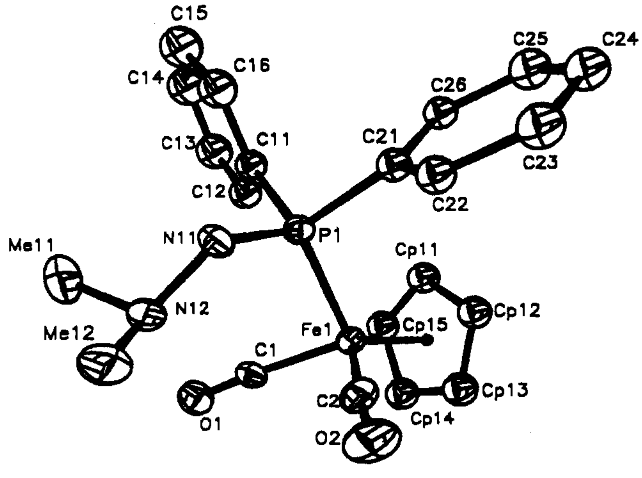
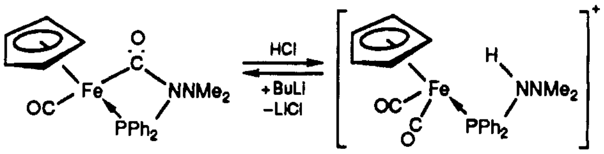


Figure 2. ORTEP view of **3** with 50% thermal ellipsoids. There are two, essentially identical, molecules per asymmetric unit. Selected averaged bond lengths (Å) and angles (deg): Fe(1)–P(1), 2.210 (4); P(1)–N(11), 1.68 (1); N(11)–N(12), 1.42 (1); Fe(1)–P(1)–N(11), 113.5 (4); P(1)–N(11)–N(12), 118.0 (8).

Table I. Crystallographic Data for **2** and **3**

	C$_{21}$H$_{21}$N$_2$O$_2$PFe (**2**)	C$_{21}$H$_{22}$IN$_2$O$_2$PFe (**3**)
fw	420.26	547.16
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	14.664 (5)	18.704 (4)
b, Å	8.0085 (9)	15.069 (1)
c, Å	17.255 (6)	18.219 (4)
β, °	110.10 (2)	117.85 (1)
vol, Å^3	1903 (1)	4540 (4)
Z	4	8
T, °C	25	25
λ, Å	0.71069 (Mo Kα)	0.71069 (Mo Kα)
ρ, g cm^{-3}	1.472	1.607
μ, cm^{-1}	8.94	21.08
$R(F_o)$	0.037	0.043
$R_w(F_o)$	0.046	0.056



(2)

Experimental Section

General Data. All manipulations were performed under an inert atmosphere by using standard techniques. All solvents were purified, dried, and distilled under nitrogen immediately prior to use. NMR spectra were obtained on a Nicolet NT-200 instrument and are referenced to external tetramethylsilane (^{1}H) or H$_3$PO$_4$ (^{31}P). IR spectra were obtained on a Perkin Elmer Model 13430 dispersive instrument as Nujol mulls.

Preparation of 2. A 0.37-g (1.23-mmol) sample of FpI in 25 mL of THF was cooled to −78 °C. To this solution was added a solution of 1.23 mmol of Me$_2$NN(PPh$_2$)Li in 20 mL of THF, producing a deep red color (the latter solution prepared by reacting equal molar quantities of n-BuLi and Me$_2$NN(PPh$_2$)H in THF at −20 °C and allowing it to stir until all of the phosphine had been deprotonated as indicated by NMR spectroscopy). The reaction was allowed to warm to room temperature, the solution turning yellow-orange in the process, and then stirred for 12 h. The solvent was removed in vacuo and the residue extracted with methylene chloride and filtered. Concentration of this solution and addition of ether resulted in the production of orange crystalline material in ca. 60% yield: ^{31}P{^{1}H} δ 116; ^{1}H(CDCl$_3$) δ 7.7 (broad, 10 H), 4.7 (s, 5 H), 3.0 (broad, 6 H); IR (Nujol) ν_{CO} = 1928, 1642 cm^{-1}. Anal. Calcd for C$_{21}$H$_{21}$N$_2$O$_2$PFe: C, 60.0; H, 5.0; N, 6.6; Found: C, 59.6; H, 4.85; N, 6.5.

Preparation of 3. A 0.5-g sample of **2** was dissolved in 25 mL of CH$_2$Cl$_2$. A saturated solution of HCl(g) in CH$_2$Cl$_2$ was slowly added until the ν_{CO} band at 1640 cm^{-1} disappeared. The solvent was removed in vacuo and recrystallized from methylene chloride/ether: ^{31}P{^{1}H}

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(7) The structure displayed here is the iodide salt of 3. This compound was produced by inadvertent halide exchange and was structurally characterized first. The chloride analogue prepared in the absence of iodide is isomorphous and was therefore not fully refined.

NMR($CDCl_3$) δ 106; ^1H NMR ($CDCl_3$) δ 7.7 (broad 10 H), 6.7 (d, $^2J_{PH}$ = 22 Hz, 1 H), 5.2 (s, 5 H), 2.4 (broad, 6 H); IR (Nujol) ν_{CO} = 2020, 1995 cm^{-1}. Anal. Calcd for $C_{21}H_{21}IN_2O_2PFe$: C, 55.2; H, 4.8; N, 6.1; Found: C, 54.8; H, 4.75; N, 5.7.

Crystallography. Crystals of **2** and the iodide salt of **3** were sealed under nitrogen in Lindeman glass capillaries and mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Crystal and data collection parameters are listed in Table I. Structures were solved by using SHELXS[8] and refined by using the SHELX system of computer programs.[9]

Acknowledgment. We wish to thank the Robert A. Welch Foundation and the Research Enhancement Program of the University of Texas at Arlington (T.C.W) and the National Science Foundation (J.L.A) for generous support of this work.

Supplementary Material Available: For **2** and **3**, tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (15 pages); tables of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.

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Reaction between $[(TPP)Ru(CO)]^{\bullet-}$ and Methyl Iodide. Evidence for Formation of a Ruthenium(II) Carbonyl Methylated Tetraphenylchlorin Derivative

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Introduction

The electroreduction of (P)Ru(CO), where P = the dianion of a given porphyrin ring, has been extensively investigated in nonaqueous media.[1-7] Two well-defined one-electron reductions are generally observed, and stable electroreduction products are obtained in virtually all nonaqueous solvents except for dichloromethane and dichloroethane, which rapidly react with the singly reduced species to give an overall irreversible electroreduction.[2,3,6]

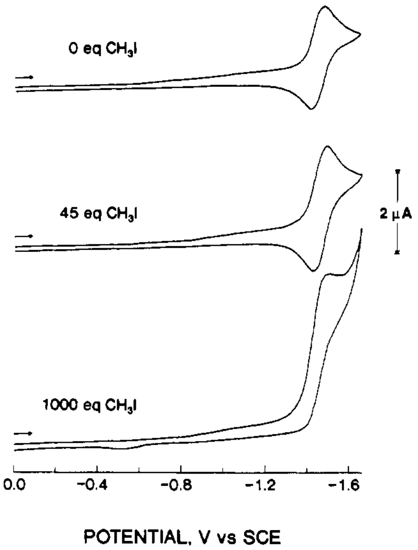

Figure 1. Cyclic voltammograms of 1.1 × 10^{-3} M (TPP)Ru(CO) in THF, containing 0.2 M TBAP and 0, 45, and 1000 equiv of CH_3I.

The first electroreduction of cobalt(II),[8] nickel(II)[9] and rhodium(III)[10,11] porphyrins is also irreversible in CH_2Cl_2 and, in the case of the cobalt and rhodium derivatives, is due to the formation of σ-bonded porphyrin complexes, as demonstrated by the isolation and characterization of $(TPP)Co(CH_2Cl)$[8] and $(TPP)Rh(CH_2Cl)$,[10] where TPP = the dianion of tetraphenylporphyrin. The formation of a CH_2Cl adduct occurs via an oxidative addition reaction that is similar to those involving alkyl or aryl halides (RX) and $[(TPP)Co)]^-$ or $[(TPP)Fe)]^-$ to give free X^- and a σ-bonded porphyrin complex of the type (TPP)M(R).[12]

σ-Bonded $(TPP)Ru(C_2H_5)$ and $(TPP)Ru(C_2H_5)_2$ complexes have also been synthesized from chemically reduced $[(TPP)Ru]_2$ and C_2H_5X,[13,14] but a reaction between chemically or electrochemically reduced (P)Ru(CO) and alkyl halides has never been reported. This was investigated in the present study for electrogenerated $[(TPP)Ru(CO)]^{\bullet-}$ and CH_3I. The resulting porphyrin product was not a σ-bonded methyl complex but rather was a methylated ruthenium(II) carbonyl chlorin. The formation of this species was monitored by in situ UV-visible and FTIR spectroelectrochemistry and the resulting final product identified by fast atom bombardment (FAB) mass spectrometry and electrochemistry.

Experimental Section

Instrumentation. Cyclic voltammetric measurements were obtained with an IBM EC 225 voltammetric analyzer. A platinum button served as the working electrode, and a platinum wire, as the counter electrode. A saturated calomel electrode (SCE) was separated from the bulk solution by a fritted-glass disk and was used as the reference electrode. Bulk controlled-potential coulometry was performed on an EG&G Princeton Applied Research Model 173 potentiostat which contained a Model 179 coulometer system that was coupled with a Princeton Applied Research Model RE0074 time base X-Y recorder. Thin-layer spectroelectrochemical measurements were made with an EG&G Princeton Applied Research Model 173 potentiostat coupled with a Tracor Northern 6500 rapid scan spectrometer. Construction of the thin-layer cell is described in the literature.[15]

Infrared measurements were carried out by using an IBM 32 FTIR spectrometer and an FTIR spectroelectrochemical cell whose construction and application have been described in the literature.[2,16] Mass spectra were recorded on a VG-70 SEQ mass spectrometer and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Materials. Reagent grade tetrahydrofuran (THF) was distilled first from CaH_2 and then from Na-benzophenone. Dimethylformamide (DMF) and benzonitrile (PhCN) were vacuum distilled from activated

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