chromatography by simple recrystallization from CH_2Cl_2/pentane. All new carbyne complexes described in this work form stable crystalline compounds which can be handled without visible decomposition in air and at room temperature. Satisfactory analytical data have been obtained for all new compounds. The results are summarized in Table I.[14]

Substitution of two carbonyl ligands in the initial tetracarbonyl carbyne complexes is possible with a variety of ligands.[9] However, nitrogenous ligands have proven particularly useful for several reasons. The amine-substituted products form in very high yields, the products are stable enough for long-term storage, and at the same time a high degree of flexibility for further substitution reactions on the carbyne complexes is maintained. For example, reaction of the bis(pyridine)-substituted complexes **3** with bis(diphenylphosphino)ethane (dppe) gives the complexes $Cl(CO)_2(dppe)W{\equiv}CR$, **11**, (**11a**, R = C_6H_5; **11b**, R = CH_3) in high yields (**11a**, 95%; **11b**, 88%).[15] Reaction of **3** with PMe_3 leads to formation of $Cl(CO)_2(PMe_3)_2W{\equiv}CPh$, **12**, in 92% yield.[15,16]

With the described reactions, stable carbyne complexes of chromium, molybdenum, and tungsten are now easily accessible. This is particularly true for the molybdenum compounds which previously could be prepared only in low yields by established routes. The wide variety of complexes attainable will provide a convenient basis for future investigations into carbyne complex chemistry.

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[14] The carbyne complexes can also be obtained from the lithium salts of the acyl complexes. This way, one-pot syntheses starting from the metal hexacarbonyls are possible; however, more extensive workup procedures due to concomitant metal hexacarbonyl are necessary.

[15] ^{13}C NMR (ppm, $CDCl_3$) and IR (cm^{-1}, CH_2Cl_2): **11a**, 267 (Cα), 213 (CO) and ν_{CO} 2003 (s), 1937 (s); **11b**, 279 (Cα), 213 (CO) and ν_{CO} 2001 (s), **12**, 266 (Cα), 212 (CO) and ν_{CO} 2000 (s), 1926 (s). The ^{13}C resonances in **11** and **12** are multiplets due to coupling with the phosphine ligands. The centers of the multiplets are given as values.

[16] Complex **12** cannot be prepared from the tetracarbonyl carbyne complex directly due to attack of PMe_3 at the carbyne carbon in $X(CO)_4WCR$. See ref 6a.

Heteronuclear Intervalent Electron Transfer in Organometallic Complexes

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Summary: Intramolecular metalation of [(dimethylamino)methyl]ferrocene with palladium chloride gives compound **2** from which the complexes **3** and **4** can be prepared. In every case, oxidation of the iron center gives an Fe(III)–Pd(II) compound which exhibits a near-infrared band for heterometal electron transfer. The band energy is dependent on the ligand L in **3**.

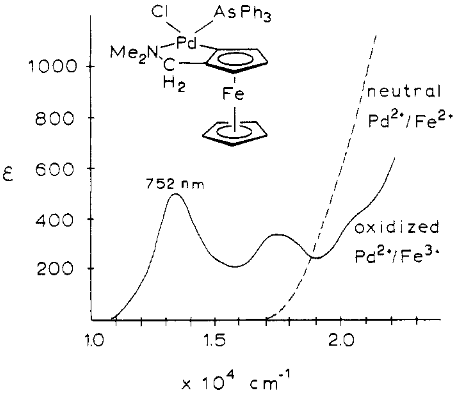

Figure 1. Near-infrared and visible spectrum of **3** (L = $AsPh_3$) before and after electrochemical oxidation at the iron center.

Numerous examples of mixed-valence organometallic compounds have been reported, but they have been limited almost entirely to compounds having two or more ferrocenyl groups, intervalent transfer being observed between Fe(II) and Fe(III).[2] With the exception of bis(fulvalene)diiron, all of the mixed-valence ferrocenyl-containing compounds described thus far are found in Hush's class II,[3] compounds with weak interaction between iron sites.

More recently, we and others have described three types of heterometal organometallic compounds that exhibit intramolecular electron transfer.[4-7] In each case, one site was a ferrocenyl group while the other was a ruthenium or cobalt ion. Unfortunately, none of these systems is amenable to significant extension, and it has been one of our goals to find organometallic mixed-valence systems within which one can make many derivatives to explore better the nature of heteronuclear intervalent electron transfer. We now wish to communicate our initial results on such a system.

If $FcCH_2NMe_2$ is allowed to react directly with $[PdCl_4]^{2-}$, complex **1** is formed,[8,9] while intramolecular metalation occurs to give **2** in the presence of a base such as sodium acetate.[10,11] The halide bridge of **2** is broken with a slight excess of ligand L (= phosphine, phosphite, pyridine, etc.) to give **3** (or **4** if L is a bidentate phosphine and $TlPF_6$ is added to precipitate the displaced Cl^-; Scheme I). The chloride ligand in **3** can be replaced in an exchange reaction. A few of the compounds synthesized thus far are given in Table I along with data pertinent to their electron-transfer properties.[12]

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[1] Exchange visitor from Fuzhou University, Fuzhou, Fujian, People's Republic of China, 1982–1983.

[2] See, for example: (a) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393. (b) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330.

[3] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

[4] Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 945, 952.

[5] Dowling, N.; Henry, P. M.; Lewis, N. A.; Taube, H. *Inorg. Chem.* **1981**, *20*, 2345.

[6] Dowling, N.; Henry, P. M. *Inorg. Chem.* **1982**, *21*, 4088.

[7] Kotz, J.; Neyhart, G.; Vining, W. J.; Rausch, M. D. *Organometallics* **1983**, *2*, 79.

[8] Fc is an abbreviation used throughout for the ferrocenyl group $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$ or $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)$.

[9] Moynahan, E. B.; Popp, F. D.; Werneke, M. F. *J. Organomet. Chem.* **1969**, *19*, 229.

[10] Sokolov, V. I.; Troitskaya, L. L.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *182*, 537.

[11] Gaunt, J. C.; Shaw, B. L. *J. Organomet. Chem.* **1975**, *102*, 511.

[12] The complexes were all prepared in good yield according to the literature (see ref 9 and 11). Except for L = $P(OEt)_3$, X = Cl and L = PPh_3, X = I or SCN, all were analyzed for C and H (and N in some cases), and all analyses were acceptable. The unanalyzed complexes all displayed cyclic voltammograms with no visible impurities, and all gave the correct number of coulombs for a one-electron process on exhaustive anodic electrolysis. The complex with L = PPh_3 and X = SCN is thought to have an S-bonded thiocyanate ligand since the C–N stretching band (at 2087 cm^{-1}) was appropriate for an S-bonded ligand.

0276-7333/85/2304-0610$01.50/0

Scheme I

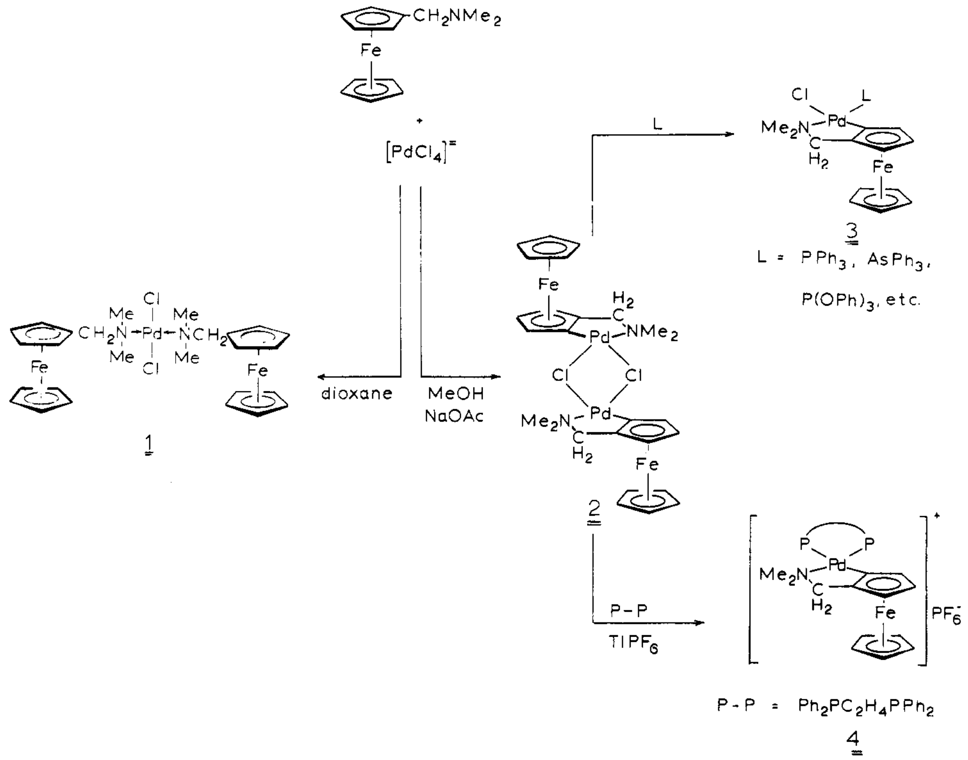

Table I. Electrochemical and Spectroscopic Data for Metalation Complexes of [(Dimethylamino)methyl]ferrocene

compound	$E_{p/2}$ (V vs. SCE) for Fe(III) → Fe(II)[a]	obsd intervalent transfer band λ, nm	 bandwidth at half-height, cm^{-1}
dimer 2	0.270	730	1887
(FcCN)PdClL (3)			
L = PPh$_3$	0.235	745[b]	2090
L = AsPh$_3$	0.240	752[c]	2060
L = pyridine	0.260	745	2340
L = P(OPh)$_3$	0.275	704	2440
L = P(OMe)$_3$	0.224	717	2120
L = P(OEt)$_3$	0.235	723	2140
(FcCN)PdX(PPh$_3$) (3)			
X = I	0.225	765	2610
X = Cl	0.235	745	2090
X = SCN	0.227	737	2230
[(FcCN)Pd(diphos)]PF$_6$ (4)	0.330	645	2759
FcCH$_2$NMe$_2$H$^+$PF$_6^-$	0.640	no IT band observed	
(C$_{10}$H$_9$FeCH$_2$NMe$_2$)$_2$PdCl$_2$ (1)	0.486	no IT band observed	
[CpFeC$_5$H$_3$CH$_2$NMe$_2$(PPh$_2$)]PdCl$_2$ (5)	0.795	no IT band observed	

[a] $I_a/I_c = 1$. The difference between anodic and cathodic peak potentials was ca. 90 mV. All complexes also had an irreversible, anodic wave at about 1.8 V attributed to oxidation of the Pd(II) site. [b] Molar absorptivity (M^{-1} cm^{-1}) = 354; λ = 736 nm in 1:1 CH$_2$Cl$_2$/CH$_3$CN. [c] Molar absorptivity (M^{-1} cm^{-1}) = 496; λ = 737 nm in 1:1 CH$_2$Cl$_2$/CH$_3$CN.

Each of the compounds of type **3** has a cyclic voltammogram consisting of an electrochemically and chemically reversible one-electron redox reaction at about +0.25 V in CH$_2$Cl$_2$ (for ferrocenyl Fe^{3+} → Fe^{2+}) and an irreversible oxidation at about +1.8 V (for Pd^{2+} oxidation) (Table I).[13,14]

The most interesting feature of the molecules studied was the electronic spectrum after bulk oxidation of a compound in CH$_2$Cl$_2$ at a potential about 200 mV more anodic than E$_{pa}$ for ferrocenyl group oxidation.[16] The spectrum in the 900–400 nm range for **3** with L = AsPh$_3$ is given in Figure 1. Two distinct bands are observed at 752 and 570 nm and a shoulder at about 475 nm. Neither of the lower energy bands is observed in the neutral complex, and both are assumed to arise from the oxidized ferrocenyl groups. Ferricenium salts characteristically have a band in the 600-nm region that has been assigned to the transition ligand e$_{1u}$ → Fe (e$_{2g}$, 3d).[4] To prove this to be

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(13) All electrochemical experiments were performed using techniques outlined in ref 7. Platinum electrodes were used, and tetrabutylammonium hexafluorophosphate was the supporting electrolyte. Virtually all experiments were done in CH$_2$Cl$_2$ or in 1:1 CH$_2$Cl$_2$/CH$_3$CN. All solvents were used as received from Burdick and Jackson. All experiments were done at room temperature (25 ± 2 °C).

(14) The potential and current for the wave at ca. +1.8 V were very sensitive to the history of the platinum electrode; a distinct wave was usually observed only on the first anodic sweep. The wave is logically assigned to oxidation of Pd(II), since we find that the benzene analogue of 2 (C$_6$H$_4$CH$_2$NMe$_2$)$_2$Pd$_2$Cl$_2$[15] displayed an irreversible anodic wave at 1.68 V, presumably for Pd(II) oxidation.

(15) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

(16) Near-infrared, visible, and ultraviolet spectra were obtained on a Cary 14 spectrophotometer at room temperature. The Fe(III)–Pd(II) complexes were all prepared by anodic electrolysis using techniques previously outlined.[7] Following electrolysis at an appropriate potential, solutions were syringed into a nitrogen-filled cuvette.

the case, the salt $FcCH_2NMe_2H^+PF_6^-$ was oxidized and its spectrum recorded. A band was observed in this case at 627 nm, and there were less intense bands at 465 and 545 nm; no bands were observed in the near infrared.

The band seen at 752 nm for **3** with L = $AsPh_3$ was observed in all such complexes (and the dimer **2**) after oxidation of the ferrocenyl group (Table I). The band is assigned as an intervalent transfer band involving the Pd(II) and Fe(III) centers for the following reasons:

(1) Neither complex **1** nor $[1,2\text{-}FcCH_2NMe_2(PPh_2)]PdCl_2$ (**5**)[17] has Pd(II) directly bonded to the ferrocenyl group. No near-infrared band is seen after oxidation of the ferrocenyl group. This is in agreement with Colbran et al., who have found that IT transitions "are only found in mixed valence ferrocene compounds when the redox sites are directly fused or bridged by electron-conducting π groups".[4]

(2) The band is sensitive to a change in solvent medium. A shift in the band maximum of 9 nm to higher energy is observed for **3** (L = PPh_3) when the solvent is changed from CH_2Cl_2 to a 1:1 mixture of CH_2Cl_2 and CH_3CN. Such shifts are expected for a mixed-valence compound of class II.

(3) According to the Hush theory of mixed-valence compounds with weakly interacting centers, the bandwidth at half-height ($\Delta\nu_{1/2}$) for an unsymmetrical ion can be determined from the expression

$$\nu_{op} - \nu_0 = (\Delta\nu_{1/2})^2/2310\ \text{cm}^{-1}$$

where ν_{op} is the energy of the IT transition and ν_0 is the internal energy difference between the two oxidation state isomers

$$\text{Fe(III)–Pd(II)} \rightarrow \text{Fe(II)–Pd(III)}$$

While ν_0 cannot be obtained directly, it has been argued that an upper limit to its value can be obtained[5,6] from the difference between the reduction potentials for

$$[\text{FcCNPdClL}]^{2+} + e^- \rightarrow [\text{FcCNPdClL}]^+$$

and

$$[\text{FcCNPdClL}]^+ + e^- \rightarrow \text{FcCNPdClL}$$

For all of the compounds of type **3**, this difference is approximately 1.5 V or 12000 cm^{-1}. This means that the bandwidth at half height should be about 1700 cm^{-1}. In fact, the half-height bandwidths are usually slightly larger than this estimate (Table I), a common observation in most mixed-valence ions.[4-7]

As seen in Table I compounds of type **3** with L as a phosphine or arsine exhibited a band in the near infrared at about 750 nm. The parent dimer **2** also gave rise to a band at 730 nm after two-electron oxidation, while **3** with L as a less basic phosphite ligand has a near infrared band nearer 700 nm. It would appear that more basic ligands L cause the intervalent transfer band to move to lower energies, a shift which may be due to stabilization of the Fe(II)–Pd(III) valence isomer. On the other hand, the cationic complex **4** (bidentate ligand = $Ph_2PC_2H_4PPh_2$) has a more energetic IT band; formation of the Fe(II)–Pd(III) valence isomer for the cationic complex is energetically unfavorable.[18]

Since the halide ligand is thought to be trans to the ferrocenyl group,[19] it is anticipated that this ligand will affect the Pd–ferrocenyl bond (owing to the so-called trans influence effect[21]) more than the cis ligand L. Thus, it is not surprising that a relatively large IT band shift is observed on changing the halide ligand from Cl to I to S-bonded SCN (when L = PPh_3).[12]

The significance of the results described is threefold. First, we have observed an intervalent transfer band for a variety of organometallic compounds having a Pd(II) center bound to an Fe(III)-containing ferrocenyl group. Thus, this series of complexes represents only the fourth class of organometallic compounds wherein intervalent transfer has been observed between two *different* metal sites. Second, the major advantage to this series of complexes is that it is capable of being greatly expanded.[22] And finally, Robin and Day in their extensive review of mixed-valence compounds noted that little was known in general about heterometal systems.[23] This series of Fe(III)–Pd(II) compounds begins to rectify that deficiency.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank Mr. Wei Lee for preparing compound **5** and Professor Kenneth Karlin and the Department of Chemistry, SUNY—Albany, for use of their NMR facilities.

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(17) Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.

(18) Note that the IT band moves to lower energy as the ligand L in **3** is changed from $P(OPh)_3$ to $P(OMe)_3$ to $P(OEt)_3$, that is, to more and more basic phosphites.

(19) When L = phosphine or phosphite, proton NMR spectra of complexes of type **3** show that each of the pair of lines assigned to the conformationally different $N\text{–}CH_3$ groups is split into a doublet, presumably owing to coupling with ^{31}P. No such splitting is observed in the spectrum of the complex when L is not a phosphine or phosphite. Since it is likely that the $^{31}P\text{–}H$ coupling constant is larger when the atoms are in the trans position than cis to one another,[20] it is believed that the ligand L is trans to the NMe_2 group, whereas X is trans to the ferrocenyl ring.

(20) As an example see: Collman, J. P.; Sears, C. T., Jr. *Inorg. Chem.* **1968**, *7*, 27.

(21) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1962**, *4*, 381.

(22) Approximately 20 complexes of the type described herein have been prepared, and all display the intervalent transfer band in the Fe(II)–Pd(II) state. These complexes will be reported in a forthcoming paper.

(23) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 248.

Generation of Dicarbonyl(η^5-cyclopentadienyl)(*trans*-2,3-dimethylcyclopropylidene)iron Trifluoromethanesulfonate and Stereochemistry of Opening to the π-Complex of 1,3-Dimethylallene

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Summary: Compound **11** has been prepared as a potential precursor to the corresponding cyclopropylidene complex **12**. Methoxy abstraction by trimethylsilyl trifluoromethanesulfonate (Me_3SOTf) at −78 °C gave the expected (by analogy with free cyclopropylidenes) ring-opened allene complex. The cyclopropylidene complex **12** could not be trapped with cyclohexene. Resolution of the intermediate carboxylic acid **9** permitted preparation of nearly optically pure **11**, which in turn gave, within experimental error, racemic allene complex **13**. This is consistent with theory that predicts the racemic allyl cation to lie between the chiral complexed carbene and its chiral allene valence isomer.

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