The stability of the μ-nitrido dimer adducts reported in this study may be attributed, in part, to the increased charge on the bridging N^{3-} atom when compared to that on O^{2-}. Knowledge of the factors responsible for this increased stability is unknown at the present time. Theoretical modeling studies as well as Mössbauer, magnetic, resonance Raman, MCD, and X-ray diffraction experiments are currently under way to more completely characterize bis ligated adducts of iron porphyrin dimers. The results of these investigations will be reported in a subsequent publication.

Acknowledgment. The support of this research from the Robert A. Welch Foundation (Grant E-680) to K.M.K., the National Institutes of Health (Grant GM 25172-02) to K.M.K. and (Grant GM 28831-01) to H.M.G., and the National Science Foundation (Grant CHE-7910305) to H.M.G. is gratefully acknowledged. L.A.B. wishes to thank the Electrochemical Society for the Weston Fellowship. We wish to thank Professor Irwin Cohen for samples of $(TPPFe)_2N$.

Registry No. $(TPPFe)_2N$, 59114-43-1; $[(TPPFe(3,5\text{-dichloropyridine}))_2N]^+$, 78591-76-1; $[(TPPFe(3\text{-cyanopyridine}))_2N]^+$, 78591-77-2; $[(TPPFe(4\text{-cyanopyridine}))_2N]^+$, 78591-78-3; $[(TPPFe(3\text{-chlorpyridinee}))_2N]^+$, 78591-79-4; $[(TPPFe(3\text{-bromopyridine}))_2N]^+$, 78591-80-7; $[(TPPFe(3\text{-acetylpyridine}))_2N]^+$, 78591-81-8; $[(TPPFe(4\text{-acetylpyridine}))_2N]^+$, 78591-82-9; $[(TPPFe(\text{aniline}))_2N]^+$, 78591-83-0; $[(TPPFe(\text{pyridine}))_2N]^+$, 78591-84-1; $[(TPPFe(3\text{-picoline}))_2N]^+$, 78591-85-2; $[(TPPFe(4\text{-picoline}))_2N]^+$, 78591-86-3; $[(TPPFe(3,4\text{-lutidine}))_2N]^+$, 78591-87-4; $[(TPPFe)_2N]^+$, 78591-88-5.

Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Indirect Metal–Metal Linkage: Cyclic Ferrocene Complexes with a Second Metal Linked via Remote Phosphine Functionality

NEIL E. SCHORE,* LINDA S. BENNER, and BRUCE E. LaBELLE

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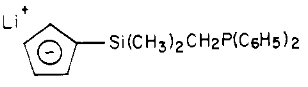
The synthesis of the heterodifunctional ligand $(C_6H_5)_2PCH_2Si(CH_3)_2C_5H_4Li$ (**1**) is described, and its utilization as a building block for the preparation of cyclic dinuclear complexes containing dissimilar transition metals is explored. The ferrocene (**2**) derived from **1** is found to coordinate with $Mo(CO)_4$, $Mn(CO)_3Br$, $NiCl_2$, $NiBr_2$, and $Co_2(CO)_6$ fragments through its two phosphine groups. Steric constraints lead exclusively to higher cyclic oligomers in the Mo and Mn complexes and have unusual stereochemical consequences in the Ni systems. The normal chemistry of the Co–Co fragment is unaffected by complexation with diphosphine **2**. An evaluation of the suitability of **1** and related ligands for the construction of different types of heterodinuclear complexes is presented.

Introduction

A most exciting development in the area of transition-metal chemistry as applied to organic synthesis has been the discovery of a number of useful transformations brought about by transition metals operating in pairs. Considerable recent evidence indicates that combinations of "early" and "late" transition metals are particularly interesting in this regard.[1] Our interest lies in the investigation of the synthesis and chemistry of molecules that simultaneously contain both "early" and "late" transition-metal functionality, so that the effects of intramolecularity on variables such as reactivity and stereochemistry may be systematically evaluated.

Our approach to the preparation of compounds containing, for example, a zirconocene-derived moiety indirectly linked to a second metal has involved the development of "heterodifunctional" ligand bridges that allow the specific and sequential attachment of dissimilar transition metals at the two ends.[2] Ideally such a ligand should be readily prepared in high yield, stable to extended storage, and capable of selective, high-yield attachment to the metals in question. The most versatile of the systems we have studied contains a cyclopentadienyl ring linked to a remote phosphine. We recently reported the synthesis of two such ligands and described the first applications of a ligand of this type in indirect metal–metal linkage.[3] The few compounds previously described containing these functional groups have seen only very limited use in transition-metal chemistry[4] and have not been shown to display the attributes most useful for this purpose.

We report here full details of the synthesis of the ligand [[dimethyl((diphenylphosphino)methyl)silyl]cyclopentadienyl]lithium (**1**) and describe the preparation of a number of complexes of its ferrocene derivative (**2**) with second metal centers. The properties of these compounds are described and compared with known systems from the point of view of ferrocene **2** as a structural model for analogues derived from metallocenes containing metals other than iron. On the basis of these results, the general utility of ligand **1** for the preparation of the desired bimetallic systems is critically evaluated.



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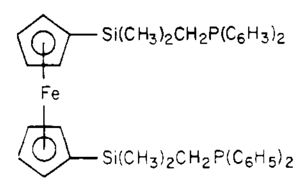

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[1] E.g.: (a) Dayrit, F. M.; Gladkowski, D. E.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3976. (b) Negishi, E.; Kukado, N. O.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, *100*, 2254. (c) Hansen, R. T.; Carr, D. B.; Schwartz, J. *Ibid.* **1978**, *100*, 2244. (d) Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1978**, 4381; *J. Am. Chem. Soc.* **1977**, *99*, 8045. (e) Negishi, E.; Van Horn, D. J. *Ibid.* **1977**, *99*, 3168. Involving nontransition metals, see: (f) Carr, D. B.; Schwartz, J. *Ibid.* **1979**, *101*, 3521. (g) Van Horn, D. E.; Negishi, E. *Ibid.* **1978**, *100*, 2252. (h) King, A. O.; Negishi, E.; Villani, F. J.; Silveira, A. *J. Org. Chem.* **1978**, *43*, 358. (i) Giacomelli, G.; Lardicci, L. *Tetrahedron Lett.* **1978**, 2831.

[2] Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251.

[3] (a) Schore, N. E. *J. Am. Chem. Soc.* **1979**, *101*, 7410. (b) Schore, N. E.; Sundar, S. *J. Organomet. Chem.* **1980**, *184*, C44.

[4] (a) Mathey, F.; Lampin, J.-P. *Tetrahedron* **1975**, *31*, 2685. (b) Mathey, F.; Lampin, J.-P. *J. Organomet. Chem.* **1977**, *128*, 297. (c) Charrier, C.; Mathey, F. *Tetrahedron Lett.* **1978**, 2407. (d) Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1979**, *170*, C41.

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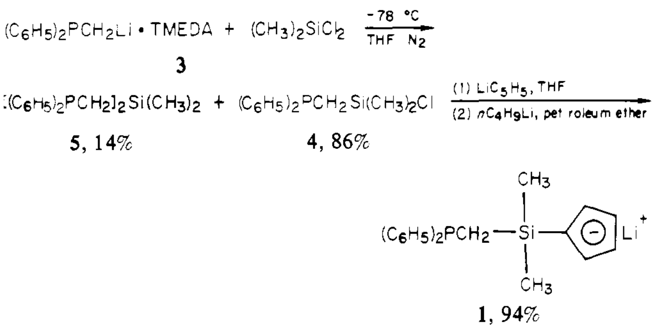
Scheme I

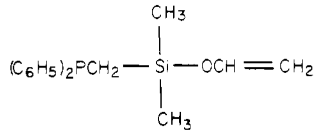


Results and Discussion

Ligand Synthesis. The starting material for ligand preparation is the tetramethylethylenediamine complex of (diphenylphosphino)methyllithium, $(C_6H_5)_2PCH_2Li{\cdot}TMEDA$ (**3**), reported by Peterson in 1967.[5] The reagent is prepared and isolated in 63% yield from the reaction of $(C_6H_5)_2PCH_3$ with a stoichiometric amount of preformed $n C_4H_9Li{\cdot}TMEDA$ in petroleum ether. Solid **3** is stable indefinitely at room temperature under nitrogen and is soluble in ethereal but not hydrocarbon solvents. Table I lists ^1H NMR data for this and all other compounds described herein.

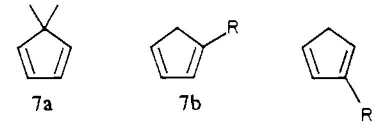
Preparation of ligand **1** is outlined fully in Scheme I. Reaction of **3** with $(CH_3)_2SiCl_2$ occurs instantaneously in tetrahydrofuran (THF) solution, giving rise to both mono- and bissubstitution products **4** and **5**. The latter greatly predominates at room temperature by a mole ratio of greater than 2:1. Although the ease of double displacement is interesting, it is not surprising in light of similar facile reactions of $(CH_3)_2SiCl_2$ with comparably hindered reagents, e.g., $(CH_3)_3SiCH_2Li$.[6] Maximization of the yield of **4** has been achieved by slowly adding a THF solution of **3** to a 15-fold excess of silane in THF, with both solutions kept at -78 °C over the course of the addition. In this way yields of 79–86% of **4** have been realized, and the small amount of byproduct **5** present causes no difficulty through the remainder of the synthesis.

Reaction of **4** with lithium cyclopentadienide proceeds smoothly and rapidly at temperatures down to -40 °C in THF. Vinyl ether **6** was found to be a minor side product when the LiC_5H_5 was prepared from butyllithium and cyclopentadiene in THF, a result of fragmentation of the solvent by the alkyllithium.[7] All three isomeric cyclopentadienes **7** are obtained from the reaction of **4** with LiC_5H_5. In THF, two NMR signals in the methyl region are observed at δ +0.07 and -0.16 in an intensity ratio of 2:5. In C_6D_6, the downfield peak is split by a solvent-induced shift. By analogy with the NMR characteristics of the isomers of cyclopentadienyltrimethylsilane,[8] the three methyl absorptions at δ +0.25, +0.19, and 0.00 (intensity ratio 1:1:5) are assigned to isomers **7c**, **7b**, and **7a**, respectively. Significantly, these cyclopentadienes are *completely inert with respect to Diels–Alder dimerization*, a quality shared with (trialkylsilyl)cyclopentadienes in general and a potential advantage over related systems possessing less bulky substitution on the ring.



$(C_6H_5)_2PCH_2Si(CH_3)_2OCH{=}CH_2$

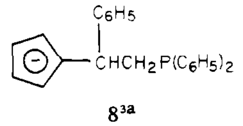
6



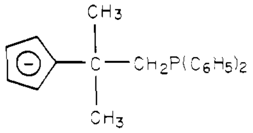
$R = Si(CH_3)_2CH_2P(C_6H_5)_2$

Deprotonation of crude mixture **7** in petroleum ether immediately results in the separation of **1** from solution as a gummy semisolid. Depending on the nature and quantity of the impurities present, it is often (but not always) possible to reduce this to a white solid by repeated vigorous washings with petroleum ether to remove possible contaminants such as **5** and **6**. The failure to remove TMEDA from crude **4** is one factor that contributes to the oily nature of some preparations of the product; nevertheless, the ligand may be stored in the form of NMR-standardized ether or THF solutions under nitrogen and gives satisfactory results in all applications. Overall yields of **1** in excess of 80%, based on **3**, may routinely be obtained.

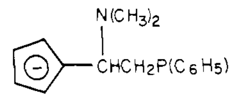
Preparation and Properties of Metal Complexes. To date, we have prepared several cyclopentadienylphosphine ligands (**8–11**) in addition to **1**. In all cases, stoichiometric attachment of the ring to appropriate metal halides (e.g., $FeCl_2$, $ZrCl_4$, $C_5H_5ZrCl_3$) proceeds with complete selectivity. All applications of ligand **1** in metal–metal linkage have therefore involved initial metal attachment to the cyclopentadienyl ring followed by attachment of a second metal to the pendant phosphine group(s).



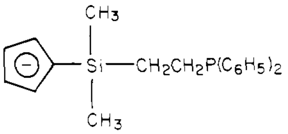
8[3a]



9[9]



10[3a]



11[3b]

Ferrocene Complex (2). Direct reaction of anhydrous $FeCl_2$ with **1** in ether affords good yields of ferrocene **2** after vigorous stirring of the heterogeneous mixture for several days followed by filtration and removal of solvent. In these preparations, evidence for a small degree of iron phosphine complex formation is observed in the broadened and shifted NMR lines and dark brown color of the crude products, but this weak form of complexation is completely broken up by rapid chromatography on alumina I. Pure **2** is isolated as a red-orange oil which only very slowly solidifes at room temperature under nitrogen. Extended contact with alumina I does lead to some decomposition and formation of methyldiphenylphosphine, which may be removed by distillation from the chromatographed product at 55 °C under high vacuum.

The purified ferrocene is air stable both in the absence of solvent and in solution and exhibits spectral characteristics

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(5) Peterson, D. J. *J. Organomet. Chem.* **1967**, *8*, 199.

(6) Petrov, A. D.; Mironov, B. F.; Ponomavenko, V. A.; Chernyshev, E. A. "Synthesis of Organosilicon Monomers"; Consultants Bureau Enterprises: New York, 1964; p 73.

(7) Presumably by reaction of THF-derived $LiOCH{=}CH_2$ with **4**: NMR (C_6D_6) δ 4.30 (d, J = 6 Hz, 1 H), 4.72 (d, J = 13 Hz, 1 H), 6.47 (dd, J = 6, 13 Hz, 1 H).

(8) (a) In C_6D_6 the methyl signals for **7** ($R = Si(CH_3)_3$) appear at δ +0.19, +0.14, and -0.11 for **7c**, **7b**, and **7a**, respectively.[8b] (b) Ashe, A. J., III *J. Am. Chem. Soc.* **1970**, *92*, 1233.

(9) Schore, N. E.; LaBelle, B. E. *J. Org. Chem.* **1981**, *46*, 2306.

Table I. Proton NMR Data[a]

compd	solvent	δ (m, *J* (Hz))			
		C_5H_4	$SiMe_2$	$SiCH_2P$	PPh_2
$LiCH_2PPh_2$·TMEDA (**3**)	THF-d_8			−0.29 (d, 3.5)	6.83–7.67 (m)
$ClSiMe_2CH_2PPh_2$ (**4**)	C_6D_6		0.42 (d, 0.95)	1.82 (br s)	7.2–7.9 (m)
$SiMe_2(CH_2PPh_2)_2$ (**5**)	C_6D_6		0.15 (t, 0.75)	1.52 (br s)	7.2–7.9 (m)
$LiC_5H_4SiMe_2CH_2PPh_2$ (**1**)	THF-d_8	5.97 (m)	0.02 (d, 0.7)	1.55 (d, 2.3)	7.10–7.67 (m)
$Fe(C_5H_4SiMe_2CH_2PPh_2)_2$ (**2**)	C_6D_6	4.12 ("t", 1.8), 4.32 ("t", 1.7)	0.34 (d, 0.9)	1.66 (d, 0.6)	7.08–7.34 (m)
	$CDCl_3$	3.98 (m), 4.23 (m)	0.14 (br s)	1.50 (br s)	7.14–7.70 (br m)
2-dioxide (**13**)	$CDCl_3$	3.93 ("t", 1.8), 4.16 ("t", 1.8)	0.28 (br s)	1.82 (d, 15)	7.2–7.9 (m)
2·$Mo(CO)_4$ (**15**)	C_6D_6	3.9–4.5 (m)	0.03, 0.18, 0.31 (s)	1.95–2.45 (br m)	7.0–8.1 (m)
2·$Mn(CO)_3Br$ (**16**)	$CDCl_3$[b]	3.82 (br s),[c] 4.14 (br s),[c] 4.03 (br s), 4.26 (br s)	−0.13 (s)	2.32,[c] 2.52 (br s)	7.33 (br s), 7.64 (br s)
2·$NiCl_2$ (**12**)	C_6D_6	4.15 (br s), 4.30 (br s)	0.75 (br s)	*d*	7.60 (br s)
	$CDCl_3$[e]	3.88, 3.90, 3.95, 4.04,[c] 4.15, 4.17, 4.19, 4.26 (s)[c]	0.62, 0.69, 0.73, 0.79 (s)[c]	*d*	see Table V
	$CDCl_3$[e,f]	3.88 (br s), 3.92, 4.05 (s),[c] 4.13 (br s), 4.18, 4.29 (s)[c]	0.24, 0.54 (s)	1.60 (br s)	see Table V
2·$NiBr_2$ (**13**)	C_6D_6	4.15 (br s), 4.30 (br s)	1.15 (br s)	*d*	4.35, 5.95, 9.50 (br s)
	$CDCl_3$[e]	3.95 (br s), 4.18 (br s), 4.05 (br s), 4.29 (br s)	1.04 (br s)	*d*	−3.9, 2.6, 4.6, 5.6, 9.4, 12.3 (br s)[b]
	$CDCl_3$[e,f]	4.03 (br m), 4.25 (br m)	0.27, 0.59 (br s)	1.93 (br s)	7.39 (br s), 7.69 (br s)
2·$Co_2(CO)_6$ (**17**)	THF-d_8	4.10 (br s), 4.28 (br s)	0.40 (br s)	2.30 (br d, 11)	7.0–7.9 (br m)
	C_6D_6	4.00 (br s), 4.20 (br s)	0.60 (br s)	2.30 (br d, 12)	7.10 (br m), 7.80 (br m)

[a] All spectra were recorded at 60 MHz and ambient temperature unless otherwise indicated. Chemical shifts are given in δ followed by multiplicity and *J* values in parentheses: "t" = apparent triplet, followed by peak-to-peak splitting. [b] 200 MHz. [c] Major signal. [d] Unobserved. [e] 360 MHz. [f] Low temperature (−55 to −60 °C).

Table II. Proton-Decoupled ^{31}P NMR Data[a]

compd	^{31}P δ	Δδ (coord)	ref
2	−30.4		*d*
2-dioxide (**13**)	+22.0		*d*
2·$Mo(CO)_4$ (**15**)	+12.3	+42.7	*d*
	+14.4	+44.8	*d*
	+24.9[b]	+55.3	*d*
cis-$Mo(CO)_4(PPh\text{-}n\text{-}Bu_2)_2$	+14.5	+40.7	19
cis-$Mo(CO)_4(PPh_2\text{-}n\text{-}Bu)_2$	+25.8	+42.9	19
trans-$Mo(CO)_4(PPh\text{-}n\text{-}Bu_2)_2$	+28.8	+55.0	19
trans-$Mo(CO)_4(PPh_2\text{-}n\text{-}Bu)_2$	+38.9	+56.0	19
2·$Mn(CO)_3Br$ (**16**)	+39.2	+69.6	*d*
	+39.6	+70.0	*d*
	+40.3	+70.7	*d*
	+40.5	+70.9	*d*
2·$NiCl_2$ (**12**)	−6.4 (−60 °C)	+24.0	*d*
	−5.5 (−60 °C)	+24.9	*d*
2·$NiBr_2$ (**13**)	+2.4[c] (−60 °C)	+32.8	*d*
2·$Co_2(CO)_6$ (**17**)	+46.3	+76.7	*d*

[a] All spectra were recorded at 81 MHz in $CDCl_3$ at 20 °C except where indicated otherwise. Chemical shifts are reported in δ: values downfield from external H_3PO_4 are positive in sign. Δδ(coord) signifies downfield shift of signal upon coordination. Only major signals are listed. [b] Minor peaks at +13.6, 13.7, 16.1, and 24.6. [c] Minor peaks at −0.7, +0.9. [d] This work.

Table III. UV/Visible Spectral Data[a]

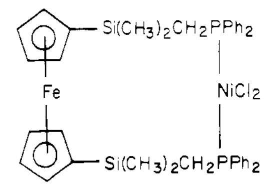
compd	λ_{max}, nm (log ε)	ref
PPh_2Et	251 (3.90), 278 (2.98)	20
ferrocene	240 (sh, 3.54), 265 (sh, 3.20), 325 (1.67), 440 (2.03)	21
2	254 (4.35), 277 (sh, 4.03), 339 (sh, 2.48), 437 (2.31)	*b*
2·$Mo(CO)_4$ (**15**)	248 (4.62), 337 (sh, 3.56), 370 (sh, 3.36), 450 (sh, 2.36)	*b*
trans-$Mo(CO)_4[P(NMe_2)_3]_2$	263 (4.45), 300 (sh), 330 (sh), 368 (3.42)	22
2·$Mn(CO)_3Br$ (**16**)	249 (sh, 4.51), 363 (sh, 2.96), 446 (3.04)	*b*
2·$NiCl_2$ (**12**)	252 (sh, 4.41), 382 (4.17), 483 (2.77), 839 (1.29)	*b*
$NiCl_2(PPh_2Me)_2$[c]	490 (2.74), 848 (1.77)	10b
$NiCl_2[PPh_2(CH_2)_3PPh_2]$[d]	469 (2.97), 820 (1.41)	10a
2·$NiBr_2$ (**13**)	248 (sh, 4.43), 317 (sh, 3.72), 408 (3.92), 507 (2.67), 854 (1.80)	*b*
$NiBr_2(PPh_2Me)_2$[c]	532 (2.46), 855 (2.26)	10b
$NiBr_2[PPh_2(CH_2)_3PPh_2]$[d]	490 (2.81), 830 (2.08)	10a
2·$Co_2(CO)_6$ (**17**)	255 (4.66), 277 (4.35), 388 (4.54), 475 (sh, 3.55)	*b*
$Co_2(CO)_6(PPh_3)_2$	393 (4.38), 450 (sh, 3.72)	23

[a] Spectra were recorded in CH_2Cl_2 at 25 °C. Only the most intense band in the 245–265-nm region is listed. [b] This work. [c] Mixture of trans and tetrahedral isomers. [d] Mixture of cis and tetrahedral isomers.

consistent with normal, unperturbed ferrocene and tertiary phosphine functionalities. Proton NMR exhibits a pair of apparent triplets near δ 4.2 typical of the AA′BB′ spectrum of 1,1′-disubstituted ferrocenes. Phosphorus-31 NMR spectrum in $CDCl_3$ exhibits a single resonance at δ −30.4 (upfield from external H_3PO_4). A very minor signal at δ +22.0 is due to the presence of a small amount of the corresponding phosphine oxide (vide infra). Both far-infrared and electronic spectroscopy show absorption characteristics of both arylphosphine and ferrocene moieties. Not surprisingly, no evidence of interaction between the metallocene portion of the molecule and the pendant phosphines is observed. Tables II–IV contain complete compilations of these data for ferrocene **2** and all its derivatives as well as for several model compounds.

Ferrocene–Nickel(II) Chloride Complex (12). Ferrocene **2** reacts with nickel halides under a variety of conditions, producing the corresponding nickel(II) halide complex. The chloride, prepared from the hydrated nickel salt in ethanol, is isolated as a brick red solid, soluble in ethers as well as halogenated and aromatic solvents. Recrystallization is possible from any of a variety of solvent mixtures such as benzene/ethanol/petroleum ether or dichloromethane/ethanol/petroleum ether. Upon standing in solutions containing hydrocarbon solvents for an extended period of time, a slightly lighter red solid is deposited which is no longer readily soluble in benzene. The analytical data are similar for the two materials, and molecular weight and spectral data indicate that, at least in chlorinated solvents, both the benzene-soluble and benzene-insoluble materials are best represented by the simple cyclic dinuclear structure **12**.

Magnetic susceptibility measurements indicate that **12** ("soluble form") exists predominantly in a diamagnetic square-planar form with a $\mu_{eff} \simeq 1.36\ \mu_B$. Variable-temper-



12

ature measurements of both ^{1}H and ^{31}P NMR spectra confirm the existence of a mobile square-planar ⇌ tetrahedral equilibrium at ambient temperature in $CDCl_3$. At −60 °C, two signals appear in the ^{31}P NMR, separated by slightly less than 1 ppm. The "soluble" and "insoluble" isomers both exhibit the same peaks but with different intensities. Warming of a solution of either isomer induces coalescence of these peaks near −40 °C, followed by further broadening such that the only signals visible in the spectra at or above room temperature are minor ones due to the free ligand and its oxide, and a very small amount of an unidentified material with δ ca. −16. At +50 °C, the free ligand signal is also broadened beyond observability.

Proton NMR reveals a very complex system indeed. Above room temperature, two major and two minor sets of aromatic proton signals can be resolved at either 200 or 360 MHz (Figure 1 and Table V). Due to broadening and overlap of neighboring peaks, these absorptions cannot all be followed much below 25 °C, but their qualitative behavior with temperatures resembles that of typical $X_2Ni(Ar_2PR)_2$ systems.[10] Thus each set of signals represents a single species undergoing relatively facile square-planar ⇌ tetrahedral interconversion at ambient temperature. Interconversion of these separate species is not observed on the NMR time scale. The "soluble" and "insoluble" forms of **12** contain different relative amounts of the individual species.

Far-IR data (Table IV) provides firm evidence for the presence of only tetrahedral and trans square-planar isomers at Ni: in addition to ligand-derived bonds, Ni–Cl stretching modes at 407 (trans), 339, and 302 cm^{-1} (both tetrahedral) appear. An unassigned band at 354 cm^{-1} raises the possibility of cis coordination. We, however, consider this unlikely due to the lack of an appropriate absorption in the low-temperature ^{31}P NMR.[14] The 354-cm^{-1} band may instead indicate the presence of a second trans isomer in the solid state possessing a different conformation of the chelating ligand.

Crystallographic methods would be the most desirable means to resolve the structural questions posed by these observations. Unfortunately, this and most of the other compounds to be described herein strongly occlude organic solvents and tend to separate as oils during attempted recrystallization. Through the use of two- and, often, three-solvent mixtures it has been possible to obtain a solid analytical sample of each of these products. However, where mixtures of isomers have been obtained as in the case of **12**, clean separations have not proved to be possible, and in no case has a crystalline product suitable for X-ray diffraction been obtained, although considerable efforts in this direction have been made and are still continuing.

In the absence of crystals suitable for X-ray diffraction, we have resorted to the use of molecular models in order to estimate the nature and severity of the steric interactions in these complexes. Dreiding models quite clearly indicate the presence of unfavorable interactions between silyl methyl groups across the center of the ring. These result in two distinct conformations for compound **12**, which are pictured in idealized form

Table IV. Far-Infrared Data[a]

compd	wavenumber, cm^{-1}	ref
2·$Mo(CO)_4$ (**15**)	625, 584, 556	*b*
trans-$Mo(CO)_4(PPh_3)_2$	629, 580	24
cis-$Mo(CO)_4(PPh_3)_2$	611, 582, 548	24
2·$Mn(CO)_3Br$ (**16**)	635, 616, 222, 203	*b*
trans-$Mn(CO)_3Br(PPh_3)_2$	637, 208	25
2·$NiCl_2$ (**12**)	407, 354, 339, 302, 260	*b*
trans-$NiCl_2(PPh_2Et)_2$	404, 265	26
cis-$NiCl_2[PPh_2(CH_2)_2PPh_2]$	379, 341, 328	27
tetrahedro-$NiCl_2(PPh_3)_2$	341, 305	27
2·$NiBr_2$ (**13**)	320, 261, 229	*b*
trans-$NiBr_2(PEt_3)_2$	327, 260	27
cis-$NiBr_2[PPh_2(CH_2)_2PPh_2]$	365, 308, 290, 266	27
tetrahedro-$NiBr_2(PPh_3)_2$	265, 232	27
2·$Co_2(CO)_6$ (**17**)	592, 424, 352, 278	*b*
$Co_2(CO)_6(P\text{-}t\text{-}Bu_3)_2$	585, 428, 380, 275	28

[a] Spectra were recorded in mineral oil mulls at 25 °C. Bands due to ligand **2** are not listed. [b] This work.

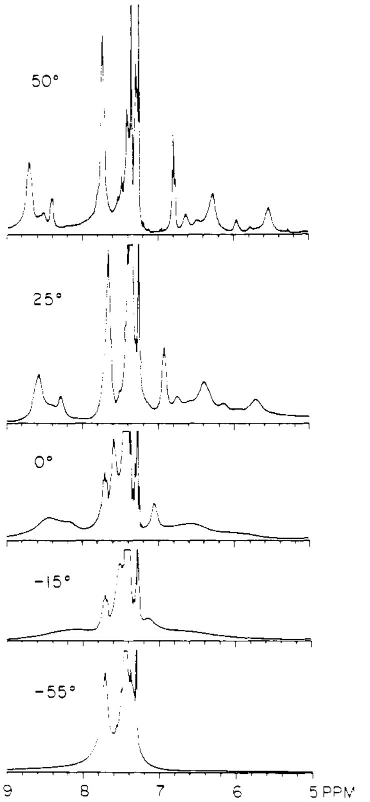


Figure 1. 360-MHz NMR of a recrystallized sample of the "benzene-soluble" form of **12**, showing the aromatic region at several temperatures.

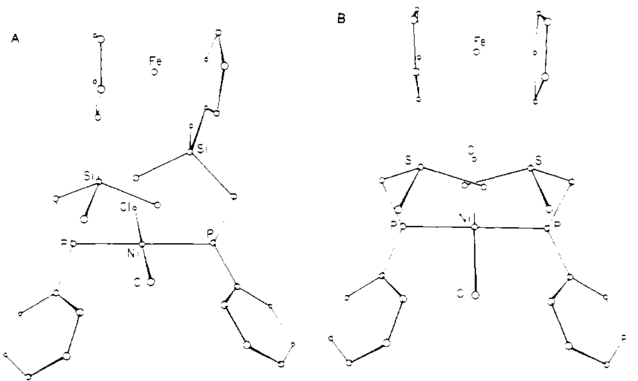


Figure 2. Two possible conformations of monomeric **12**: left, conformation "A"; right, conformation "B" (see text). One phenyl group has been removed from each phosphorus atom for clarity.

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[10] (a) Van Hecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966**, *5*, 1968. (b) Pignolet, L. H.; Horrocks, W. D., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 1855. (c) La Mar, G. N.; Sherman, E. O. *Ibid.* **1970**, *92*, 2691.

Table V. Aromatic Proton Signals of **12** at 360 MHz in $CDCl_3$[a]

temp, °C	δ, meta	δ, ortho	δ, para
		Species "A"	
50	7.73	7.40	6.79
25	7.65	7.40	6.91
0	7.58	ca. 7.42	7.05
		Species "B"	
50	8.70	6.27	5.52
25	8.58	6.39	5.71
0	ca. 8.44	ca. 6.55	ca. 6.03
		Species "C"	
50	8.40	6.62	5.95
25	8.28	6.75	6.14
0	ca. 8.17	ca. 6.88	*b*
		Species "D"	
50	8.55	6.47	5.77
25	8.39	6.61	5.95

[a] Species "A" and "B" are the major components present.
[b] Unobservable.

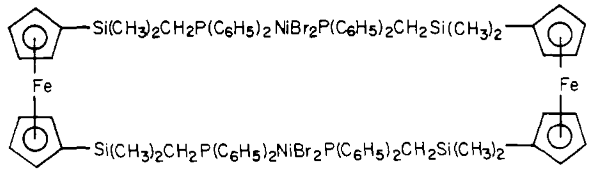
in Figure 2. Both possess parallel P-Ni-P and Cp-Fe-Cp bond axes, one (conformation "A") with an axis of symmetry containing the two metal atoms and the other ("B"), a mirror plane defined by the two metals and the two halogens. As drawn, these conformations exhibit unfavorable methyl-methyl interactions which may be relieved at no steric expense by twisting about the Cp-Fe-Cp axis. Interconversion of the model conformations requires rotation about one (Cp ring) C-Si bond, a motion that appears to be quite difficult in the intact cyclic system in the absence of substantial bond deformation.

The observation of two solid-state forms of **12** and two major solution isomers which do not interconvert on the NMR time scale at ambient temperature would ordinarily be most easily explained by a very slow monomer-dimer equilibrium. Neither osmometric measurements in $CHCl_3$ nor field-desorption mass spectroscopy (FDMS) show any evidence, however, for the presence of significant quantities of dimers or higher oligomers in either solid-state form of **12**. There may be artifactual reasons for this. Nevertheless, the models do supply an alternative explanation, namely, the possibility of two monomeric conformations that interconvert only with great difficulty. Conformationally distinct solid-state isomers have, in fact, been reported for the nickel(II) chloride complex of 1,2-bis(diphenylphosphino)ethane.[11] These also display different physical properties including different Ni-Cl stretching frequencies in the far-IR. However, in the absence of more direct structural studies, these questions involving the nature of **12** must remain unresolved.

Ferrocene-Nickel(II) Bromide Complex (13). The corresponding nickel bromide complex **13** has been prepared by reaction of anhydrous $NiBr_2$ and ferrocene **2** in benzene. The somewhat greenish brown powdery product possesses a μ_{eff} = 1.93 μ_B at 25 °C, somewhat larger than the chloro compound but smaller than typical nickel(II) bromide complexes of alkyldiarylphosphines.[10] The ^1H and ^{31}P NMR spectra at −60 °C are less complex than those of the chloro compound. The proton spectrum can be interpreted as a superposition of the complete spectrum of a diamagnetic species and a partial spectrum (cyclopentadienyl ring and silyl methyl protons only) of the tetrahedral form, the two isomers being present in approximately a 2:1 ratio. The latter agrees well with the mole fraction of tetrahedral isomer, $N_T = 0.30$, derived from the μ_{eff} value and corrected for the change in temperature according to the relationship $N_T = [\exp(\Delta G/RT) + 1]^{-1}$. Only one major peak appears in the ^{31}P NMR, at δ 2.4, and this evidence, together with far-IR data, is reasonably interpretable as resulting from a mixture of predominantly trans square-planar and tetrahedral isomers.

At higher temperatures the proton NMR becomes considerably more complicated, with the room-temperature spectrum taking on the general appearance expected based on analogous systems with nonchelating ligands. Major absorptions due to ferrocene ring protons, silyl methyl groups, and phenyl hydrogens of a single species dominate the spectrum, although additional absorptions typical of phenyl hydrogens suggest the presence of a second, independent, equilibrating system. Part of the difficulty in interpretation is due to the small concentration of tetrahedral isomer which, as in the case of the chloride, makes it impossible to locate all of the signals due to its aromatic protons at −60 °C. Only a single, severely broadened feature located at ca. δ 25.5 is visible outside of the δ 0–10 region at this temperature. The ^{31}P spectrum is too broad to be detected at all above −20 °C.

Like **12**, **13** analyzes as monomeric in chloroform osmometrically. FDMS measurements at slightly elevated emitter temperatures, however, show clear evidence for dimers, with peaks in the *m/e* 1830–1836 region. Although interpretation is complicated by the fact that visible decomposition occurs under these conditions, it appears most likely that **13** is a mixture consisting predominantly of a single monomer in the presence of some dimeric material (presumably of structure **14**) both in the solid state and in solution.



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Ferrocene-Molybdenum Carbonyl Complex (15). Reaction of ferrocene **2** with norbornadiene molybdenum tetracarbonyl[12] in refluxing methylcyclohexane gives rise, after purification, to a yellow solid in 30% yield that analyzes as ferrocene **2** plus $Mo(CO)_4$ plus 0.5 petroleum ether. Spectroscopically, the presence of a mixture is again indicated by both NMR and IR data: the most intense IR band in the carbonyl region at 1870 cm^{-1} is characteristic of a *trans*-$Mo(CO)_4(Ph_2PR)_2$ fragment as being the major constituent, although the presence of appreciable quantities of the cis isomer is indicated by bands at 1915 and 2012 cm^{-1}. A very small quantity of a $Mo(CO)_5(Ph_2PR)$ species is suggested by very weak bands at 1941, 1953, and 2067 cm^{-1}. The presence of an intact ferrocene unit in **15** is indicated by a shoulder in the visible spectrum at ca. 450 nm (ϵ ~230) and ^1H NMR bands in the δ 4–4.5 region. The asymmetric nature of the latter and the presence of three singlets in the $SiCH_3$ region confirm the presence of a mixture, as does the ^{31}P NMR, which displays an array of at least seven absorptions in the region δ 10–25 downfield from H_3PO_4, with major signals at δ 12.3, 14.4, and 24.9 (Table II). Molecular weight determination in $CHCl_3$ gives a value of ca. 1850, or about twice the monomeric formula weight. The dimeric nature of **15** is confirmed by FDMS.

Values of $\Delta\delta$(coord), the difference in ^{31}P chemical shift between the coordinated and the free ligand, are presented in Table II for this system and for several simple molybdenum carbonyl phosphine complexes. The signals present in the NMR of **15** display $\Delta\delta$(coord) values characteristic of both *cis*- and *trans*-$Mo(CO)_4(PR_3)_2$ systems in general, consistent

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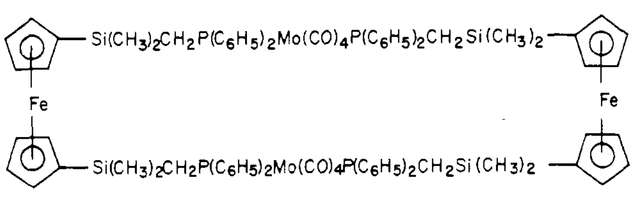
(11) Udovich, C.; Takemoto, J.; Nakamoto, K. *J. Coord. Chem.* **1971**, *1*, 89.

(12) King, R. B. *Inorg. Chem.* **1963**, *5*, 936.

with the IR results. Together with the molecular weight data, this evidence suggests that **15** is primarily a mixture of three "dimeric" species, **15a–c**, with smaller amounts of higher oligomers giving rise to the minor absorptions in the ^{31}P NMR spectra. Attempts to separate a major component from this mixture in pure form have been unsuccessful. The trans–trans isomer appears to be slightly more soluble in CH_2Cl_2/petroleum ether than are the other components (IR), but only partial enrichments have been achieved.



15a, both Mo trans
b, one cis, one trans Mo
c, both Mo cis

Ferrocene–Manganese Carbonyl Bromide Complex (16). This material is obtained in 40% yield as a yellow solid upon reaction of solid $BrMn(CO)_5$[13] with a refluxing benzene solution of ferrocene **2**. As in the case of **15**, a mixture of isomers is suggested by both IR and NMR spectroscopy. The 200-MHz proton NMR gives evidence for two distinct sets of ferrocene absorptions in a 7:1 intensity ratio. Four major IR absorptions appear in the carbonyl region at 1897 (vs), 1939 (vs), 1958 (s), and 2029 (m) cm^{-1}, consistent with the presence of both cis (*fac*) and trans (*mer*) substitution in the $BrMn(CO)_3(Ph_2PR)_2$ units. Two bands appear in the Mn–Br stretch region of the far-IR spectrum at 203 and 222 cm^{-1}. Again, molecular weight determination gives rise to an unusually large value of 2200, more than twice the monomeric formula weight. It is likely that **16** is a mixture of compounds analogous to the structures proposed for molybdenum complexes **15**. Phosphorus-31 NMR spectra show four peaks centered about δ +40; the literature contains very little data for direct comparison.

The exclusively oligomeric natures of both **15** and **16** appear to result from ligand-derived steric interactions similar to those proposed for nickel complex **12**. In particular, coordination of an octahedral metal fragment to **2** results (Dreiding models) in unavoidable interference of at least one ligand on that metal with the silyl methyl groups of the ligand in near-idealized conformations (cf. Figure 1). These interactions may be relieved by twisting about the ferrocene ring–metal bonds, but this reduces the metal–metal distance from a maximum of nearly 6 Å to under 5 Å and simultaneously introduces crowding of the ligands on the second metal into the ferrocene moiety itself. Monomeric complexes of **2** with octahedral metal fragments would appear to be inaccessible due to these steric interactions.

Ferrocene–Cobalt Carbonyl Complexes (17). A rapid reaction takes place between **2** and $Co_2(CO)_8$ in benzene at room temperature to give rise to two products, both brown solids, each in 35–40% yield, one soluble and one insoluble in the reaction mixture. As in the case of the soluble and insoluble isomers of the nickel chloride complex described above, these materials appear to be very similar spectroscopically: in THF their IR spectra are identical, with major carbonyl bands at 1969 (m, sh) and 1952 (vs) cm^{-1}, characteristic of the presence of the $CH_2P(C_6H_5)_2Co(CO)_3Co(CO)_3P(C_6H_5)_2CH$ structural unit in both species.[14] No IR evidence for the presence of an ionic species of the general formula $CoL_2(CO)_3{}^+Co(CO)_4{}^-$ is obtained at any stage of the preparation or isolation of **17**. The ^1H NMR spectra of the two products are very similar; in particular, both materials display broad doublets at δ 2.30 (J = 11–12 Hz) for the CH_2P protons. Phosphorus NMR further indicates the identity of these materials in $CDCl_3$ solution, with both showing a single absorption at δ +46.3. Upon standing, a benzene solution of the more soluble material slowly deposits a precipitate of the insoluble modification. Molecular weight determinations in $CHCl_3$ were somewhat complicated by slow decomposition of the complexes; nonetheless, values of 1020 for the more soluble and 1180 for the less soluble products were obtained (the monomeric formula weight is 985). Within experimental error, both materials are therefore largely or completely monomeric in solution. The occurrence of two distinct forms of compound **17** may well be an additional example of conformationally derived isomerism in the solid state.

Chemical Behavior. Both isomers of **17** are very sensitive to oxygen in solution. Bubbling of air through a $CHCl_3$ solution of **17** rapidly discharges the brown color characteristic of the hexacarbonyldicobalt diphosphine moiety, ultimately leading to a dark green precipitate and an orange solution. The supernatant displays a single visible absorption at 449 nm, and after removal of solvent, gives rise to an orange solid whose spectral characteristics are completely consistent with the bis(phosphine oxide) **18** of ferrocene **2** (e.g., NMR δ 1.82 (d, J = 15 Hz for $CH_2P(O)<$)).

Reduction of a THF solution of **17** has been attempted in two ways. The standard method, using dilute sodium amalgam, gives rise to greenish solutions displaying IR bands at 1925 (m), 1885 (s, br), and 1850 (s) cm^{-1}. Only the first and third bands are expected for the desired anionic species, and the presence of the intense absorption around 1885 cm^{-1} is suggestive of the presence of $NaCo(CO)_4$. A dark precipitate also accompanies this reduction process. An alternate, cleaner method for reductive cleavage of the metal–metal bonds in hexacarbonyldicobalt diphosphines utilizes potassium hydride as the reagent.[15] Reaction of **17** with the appropriate amount of KH in THF gives rise to an olive green solution with major IR bands at 1924 (s), 1890 (w), 1844 (vs), and 1816 (m, sh) cm^{-1}. Although decomposition to $KCo(CO)_4$ and a green precipitate is observed during the course of this process, it is no longer a major problem as in the Na/Hg procedure. Addition of bis(triphenylphosphine)iminium chloride precipitates KCl and produces a yellow solution of, predominantly, the salt **19**, contaminated with a small amount of $Co(CO)_4{}^-$: IR (THF) 1921 (s), 1883 (s), 1835 (vs) cm^{-1}. These IR data are nearly identical with those for $Co(CO)_3P(C_6H_5)_3{}^-PPN^+$ under similar conditions.[15]

These transformations demonstrate the effective chemical independence of the two metal sites. Both oxidation and reduction reactions occur at the $Co_2(CO)_6L_2$ moiety without any evidence for unexpected chemical transformations at the ferrocene site (Scheme II). Thus the reactivity differences expected on the basis of the known chemistry of ferrocene and cobalt carbonyl derivatives individually are preserved, at least qualitatively, in the cyclic binuclear complex.

Implications. The use of ligands possessing both cyclopentadienyl and phosphine functionality allows different metal fragments to be complexed in a specific, directed manner.[3a] The suitability of any individual such ligand for construction of complexes displaying specific spatial relationships between two metal centers has been shown here to be a sensitive function of the ligand structure. Ligand **1**, as incorporated into ferrocene **2**, is revealed to be an excellent building block for macrocyclic, polynuclear systems of a type only rarely

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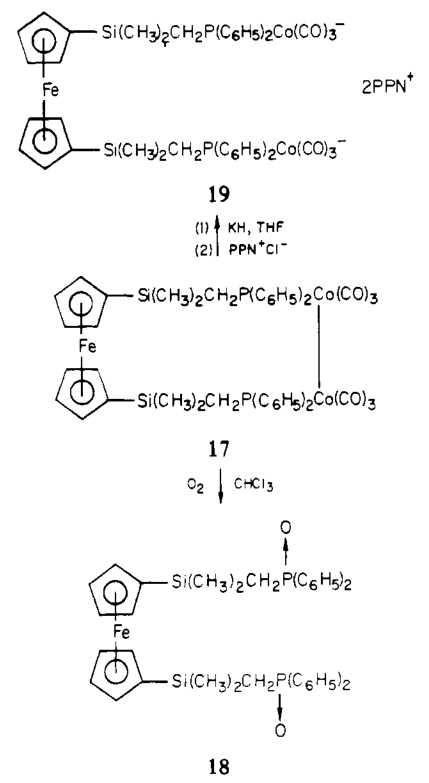
(13) Quick, M. J.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 160.

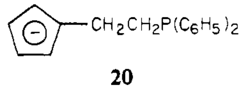
(14) McCleverty, J. A.; Davison, A.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3890. Manning, A. R. *J. Chem. Soc. A* **1968**, 1135.

(15) Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organomet. Chem.* **1978**, *154*, 337.

Scheme II



encountered in transition-metal systems (e.g., **15** and **16**).[16,17] The suitability of **2** in the construction of simple monomeric cyclic complexes is, on the other hand, clearly quite limited. Ligands that should be well suited to the latter purpose (based, again, on the examination of models) include Mathey's ethano-bridged ligand **20**,[4d] and the two-methylene analogue of **1**, ligand **11**.[3b] We have begun a study of metallocenes derived from ligand **11** and have obtained preliminary results that indicate that the chemistry will be considerably less complex than that of ferrocene **2**. Models indicate much greater flexibility in bimetallic complexes of **11** relative to **1**, with a very wide range of metal–metal distances available due to the greater conformational mobility of the system. We feel that bimetallic systems derived from ligands such as these will serve as powerful models for the study of chemical and physical interactions between proximate transition-metal centers.



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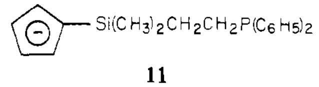

11

Experimental Section

General Data. All preparations were carried out under an atmosphere of N_2 by using either standard Schlenk techniques or a Vacuum Atmospheres DriLab. Where suitable, solvents were rendered water and oxygen free by distillation from sodium benzophenone ketyl or dianion. Halogenated solvents were dried over 3A molecular sieves and degassed before use. Methyldiphenylphosphine and dicobalt octacarbonyl were obtained from Pressure Chemical Corp. and used as received. $BrMn(CO)_5$[13] and $Mo(CO)_4$(norbornadiene)[12] were prepared by literature methods. All other organic reagents were redistilled under N_2 and degassed before use. Solid inorganic reagents were obtained from Alfa/Ventron and transferred into the drybox after being held at high vacuum for at least 12 h. Spectroscopic measurements utilized the following instrumentation: UV/visible, Cary 17; IR/far-IR, Beckman IR-8, Perkin-Elmer 180; ^{1}H NMR, Varian A60-A, Nicolet NT-200, Nicolet NT-360; ^{31}P NMR, Nicolet NT-200 (at 81 MHz). Molecular weight determinations were carried out in $CHCl_3$ with the use of a Mechrolab 301A vapor pressure osmometer with $(C_6H_5)_3SbCl_2$ as the standard. Elemental analyses were carried out by the Galbraith Microanalytical Laboratory or the U.C. Berkeley Microanalytical Laboratory. Field-desorption mass spectroscopy experiments were carried out at the Bio-organic, Biomedical Mass Spectrometry Resource of the U.C. Berkeley Space Sciences Laboratory.

(Diphenylphosphino)methyllithium–TMEDA Complex (3). A solution of 22.5 mL of 2.2 M *n*-butyllithium (50 mmol) in 35 mL of petroleum ether was treated dropwise with 5.8 g (50 mmol) of TMEDA at 27 °C under N_2. Then 10.0 g (50 mmol) of methyldiphenylphosphine was added and the mixture stirred for 72 h. The precipitated yellow product (11.5 g, 63%) was isolated by filtration under N_2 followed by washing with 3 × 20 mL of petroleum ether. NMR (THF-d_8): δ −0.29 (d, J = 3.5 Hz, 2 H), 2.22 (s, 12 H), 2.39 (s, 4 H), 6.83–7.67 (m, 10 H).

Chlorodimethyl((diphenylphosphino)methyl)silane (4). A solution of 35 g (270 mmol) of dichlorodimethylsilane in 25 mL of THF was cooled to −78 °C under N_2. To this rapidly stirred mixture was added over a period of 1 h a solution of 6.9 g (19 mmol) of **3** in 110 mL of THF which was also held at −78 °C throughout the addition. After the mixture was warmed to 25 °C, solvent was removed in vacuo, leaving a yellowish oily semi-solid. Trituration with 3 × 50 mL of petroleum ether allowed removal of LiCl by filtration, and both solvent and TMEDA were then removed at high vacuum. (Complete removal of TMEDA is required at this juncture if the final product of the sequence is to be isolated in pure form.) A yellowish oil weighing 5.7 g was obtained which consisted of 0.6 g (14%) of dimethylbis((diphenylphosphino)methyl)silane, **5**, and 5.1 g (86%) of **4**. NMR of **5** (C_6D_6): δ 0.15 (t, J = 0.75 Hz, 6 H), 1.52 (br s, $w_{1/2}$ = 1.4 Hz, 4 H), 7.2–7.9 (m, 20 H). NMR of **4** (C_6D_6): δ 0.42 (d, J = 0.95 Hz with Si^{29} satellites, J = 0.95 and 7.15 Hz, 6 H), 1.82 (s, $w_{1/2}$ = 1.0 Hz, 2 H), 7.2–7.9 (m, 10 H). This mixture was used without further purification.

[Dimethyl((diphenylphosphino)methyl)silyl]cyclopentadiene (7). Lithium cyclopentadienide was prepared and isolated in the drybox as follows. A cooled (−40 °C) solution of 2.44 g (37 mmol) of cyclopentadiene in 50 mL of diethyl ether was treated carefully, dropwise, with 14.8 mL of 2.2 M *n*-butyllithium (33 mmol). The precipitated LiC_5H_5 was collected, washed with 3 × 10 mL of ether, and dried under N_2, yield 2.6 g (109%, contains occluded ether).

A solution of 5.1 g of the mixture of **4** and **5** (containing 4.6 g or 15 mmol of **4**) in 30 mL of THF (NMR δ 0.28) was cooled to −40 °C and treated with a similarly cooled solution of ca. 1.2 g of LiC_5H_5 in 30 mL of THF under N_2. The reaction was monitored by NMR spectroscopy and the addition stopped when the signal at δ 0.28 had been completely replaced by several new resonances. Solvent was removed in vacuo, and the residue triturated with 30 mL of petroleum ether and filtered. The solids were washed with 3.6 mL of petroleum ether, and solvent was removed from the combined filtrates in vacuo. The resulting oil weighed 5.6 g and contained ca. 5.1 g (100%) of a ca. 2.5:1 mixture of isomers of **7**: NMR (THF) δ −0.16 (d, J = 0.9 Hz) for major isomer **7a** and 0.07 (d, J = 0.8 Hz) for minor isomers **7b** and **7c**, also δ 6.5 (br, ca. 3–4 H) and 7.1–7.7 (m, 10 H). This mixture was also used directly in the next step.

[[Dimethyl((diphenylphosphino)methyl)silyl]cyclopentadienyl]lithium (1). A solution containing the above mixture of isomers (ca. 5.1 g **7**, 15 mmol) in 35 mL of petroleum ether was treated, dropwise, with 7.2 mL of 2.2 M *n*-butyllithium (15 mmol) at 27 °C under N_2. A gummy orange-brown material immediately separated from solution. The supernatant was drawn off and shown to contain aromatic material (presumably **5**) by NMR spectroscopy. Fresh petroleum ether (ca. 20 mL) was added, the mixture vigorously stirred for several hours, and the supernatant drawn off. This procedure was repeated several times, eventually resulting in a nearly pure white powdery product;

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(16) A few related systems utilizing bis (group 5 element) ligands have been reported: Fukumoto, T.; Matsumura, Y.; Okawara, R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 711. Beall, T. W.; Houk, L. W. *J. Organomet. Chem.* **1973**, *56*, 261. Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59. Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373.

(17) These macrocyclics appear to be sufficiently flexible to allow interaction between the two metal carbonyl fragments across the center of the ring. Possible chemical consequences of this are being explored.

yield 4.9 g (94%). (For NMR data, see Table I.)

1,1′-Bis[dimethyl((diphenylphosphino)methyl)silyl]ferrocene (2). A suspension of 0.41 g (3.25 mmol) of anhydrous iron(II) chloride in 5 mL of ether was treated with a solution of 2.15 g (6.54 mmol) of **1** in 20 mL of ether and the mixture stirred at 27 °C under N_2 for 2 days. Insoluble material was removed by filtration and washed with 4 × 10 mL of ether. The combined filtrates were reduced to a brown oil at high vacuum. This oil was chromatographed (alumina I/benzene) yielding an orange-red oil which solidifed after storage for several months under N_2. Washing with a little cold petroleum ether yielded 1.9 g (85%) of a red solid, mp 53–56 °C. Anal. Calcd for $C_{40}H_{44}P_2Si_2Fe$: C, 68.76; H, 6.35; Si, 8.04; Fe, 7.99. Found: C, 68.69; H, 6.46; Si, 7.97; Fe, 8.13. IR (mineral oil mull): 1300 (w), 1247 (m), 1162 (m), 1078 (w), 1034 (m), 1023 (w), 805 (s, br), 737 (m), 692 (s) cm^{-1}.

$Fe[C_5H_4Si(CH_3)_2CH_2P(C_6H_5)_2]_2NiCl_2$ (12). A solution of 0.08 g (0.34 mmol) of nickel(II) chloride hexahydrate in 20 mL of absolute, N_2-purged ethanol was heated to reflux under N_2, treated dropwise with a solution of 0.24 g (0.34 mmol) of **2** in 10 mL of a 1:1 benzene/ethanol mixture, and refluxed for an additional 30 min. The cooled reaction mixture was taken to dryness under vacuum and the residue washed with several small portions of petroleum ether to remove unreacted **2**. A quantitative yield (0.28 g) of crude product, a brick red solid, was obtained. A portion of this product was recrystallized by dissolution in CH_2Cl_2 and treatment with a 1:1 ethanol/petroleum ether mixture, followed by refrigeration. The resultant dark red precipitate was benzene-soluble and had a melting point of 105–108 °C. Molecular weight for **12**: calcd, 828; found (osmometric), 850 ± 50. (FDMS at 10 mA: 828 (1), 698 ($\mathbf{2}^+$, 65), 697 (100).)

Another portion of the crude product was recrystallized with the use of a similar technique, replacing the CH_2Cl_2 with benzene in the hope of increasing the recovery of material. Precipitation of a light red solid occurred at −40 °C over an extended period of time; recovery 75%, mp 135–137 °C. Material precipitated from benzene with petroleum ether alone is similar in nature. Anal. Calcd for $C_{40}H_{44}P_2Si_2FeNiCl_2{\cdot}C_6H_6$: C, 60.95; H, 5.56; P, 6.83; Cl, 7.82. Found: C, 60.52; H, 5.66; P, 6.84; Cl, 7.85. Molecular weight for **12**: calcd, 828; found (osmometric), 815 ± 50.

$Fe[C_5H_4Si(CH_3)_2CH_2P(C_6H_5)_2]_2NiBr_2$ (13). A suspension of 0.05 g (0.22 mmol) of anhydrous nickel(II) bromide in 5 mL of dry benzene was treated under N_2 with a solution of 0.16 g (0.22 mmol) of **2** in 5 mL of benzene. After 48 h of stirring, unreacted $NiBr_2$ was removed by filtration and solvent removed from the filtrate. The residue was thoroughly washed with petroleum ether to remove unreacted **2**. The residue, which is soluble in benzene, slightly soluble in absolute ethanol, and essentially insoluble in petroleum ether, was recrystallized from a mixture of these three solvents, yielding 0.07 g (36%) of **13**, a brown powder; mp 126–129 °C. Anal. Calcd for $C_{40}H_{44}P_2Si_2FeNiBr_2{\cdot}0.5C_2H_5OH$: C, 51.16; H, 4.92; Br, 16.59. Found: C, 51.69; H, 4.97; Br, 15.52. Molecular weight for **13**: calcd, 917; found (osmometric), 865 ± 50. (FDMS at 14.5 mA: 1836 (13), 1834 (19), 1832 (14), 1831 (21), 918 (2), 917 (7), 916 (20), 913 (5), 912 (14), 699 (29), 698 ($\mathbf{2}^+$, 80), 697 (100).)

$Fe[C_5H_4Si(CH_3)_2CH_2P(C_6H_5)_2]_2Mo(CO)_4$ (15). A mixture of 0.12 (0.41 mmol) of (norbornadiene)tetracarbonylmolybdenum and 0.27 (0.38 mmol) of **2** in 45 mL of methylcyclohexane was refluxed under N_2 for 1.5 h. After removal of solvent, the residue was taken up in 2 mL of dichloromethane, filtered, treated with 6 mL of petroleum ether, and cooled to −40 °C. The brownish semi-solid that separated out was dissolved in 2 mL of benzene, filtered, and taken to dryness in vacuo, yielding 0.11 g (30%) of **8** as a yellow-orange solid. After dissolution in ether and precipitation with petroleum ether (−40 °C), the light yellow solid obtained does not display a clear melting point but begins to soften at 100 °C, gradually becoming an orange, viscous semi-solid at ca. 117 °C. Further heating causes no visible change until decomposition (gas evolution) is observed at 170 °C. Anal. Calcd for $C_{88}H_{88}P_4Si_4Fe_2Mo_2O_8{\cdot}C_5H_{12}$: C, 59.19; H, 5.30; P, 6.57. Found: C, 59.28, 59.39; H, 5.04, 5.32; P, 6.08. Molecular weight for **15**: calcd (dimeric), 1814; found (osmometric), 1850 ± 200. (FDMS at 15 mA 1816 (2), 1605 (4); FDMS at 13.5 mA 910 (1), 909 (1), 908 (8), 907 (5), 906 (1), 905 (14), 904 (3), 903 (2), 902 (15), 900 (3), 699 (15), 698 ($\mathbf{2}^+$, 47), 697 (100).) UV/vis (CH_2Cl_2): λ_{max} (log ϵ) 248 (4.62), 254 (4.61), 260 (4.58), ca. 337 (sh, 3.56), ca. 450 (sh, 2.36) nm. IR (mineral oil mull): 2067 (vw), 2012 (w), 1953 (sh), 1915 (sh), 1872 (vs, br), 1302 (m), 1250 (w), 1160 (m), 1090 (vw), 1037 (vw), 1019 (w), 890 (w), 804 (w), 737 (sh), 694 (w), 625 (sh) cm^{-1}.

$Fe[C_5H_4Si(CH_3)_2CH_2P(C_6H_5)_2]_2Mn(CO)_3Br$ (16). A mixture of 0.08 g (0.29 mmol) of bromopentacarbonylmanganese(I) and 0.21 g (0.29 mmol) of **2** in 25 mL of benzene was refluxed under N_2 for 3.5 h during which time the solid $Mn(CO)_5Br$ dissolved, giving an orange solution. After removal of solvent, the residue was thoroughly washed with petroleum ether, dissolved in a minimum amount of benzene, treated with ethanol until just cloudy, and finally diluted with ca. 3 volumes of petroleum ether. The resultant mixture was refrigerated yielding after 3 days 0.11 g (40%) of **9**, a yellow solid, mp 144–147 °C (darkened above 135 °C). Anal. Calcd for $C_{86}H_{88}P_4Si_4Fe_2Mn_2O_6Br_2$: C, 56.28; H, 4.83; Br, 8.71. Found: C, 54.73; H, 4.95; Br, 8.40. Molecular weight for **16**: calcd, 1836; found (osmometric), 2200 ± 200. IR (mineral oil mull): 2080 (vw), 2029 (m), 1958 (s), 1939 (vs), 1896 (vs) cm^{-1} (ν_{CO}).

$Fe[C_5H_4Si(CH_3)_2CH_2P(C_6H_5)_2]_2Co_2(CO)_6$ (17). A filtered solution of 0.12 g (0.36 mmol) of octacarbonyldicobalt in 45 mL of benzene was treated dropwise with a solution of 0.24 g (0.34 mmol) of **2** in 5 mL of benzene. After 1 day at room temperature, a brown precipitate had formed. The solution was filtered and solvent removed in vacuo, leaving a red-brown solid. This solid was redissolved in benzene, the solution refiltered as it did not completely dissolve, and the solution treated with twice its volume of petroleum ether. A brown solid was collected, 0.13 g (39%), mp 130 °C dec. Anal. Calcd for $C_{46}H_{44}P_2Si_2FeCo_2O_6$: C, 56.11; H, 4.50. Found: C, 54.76; H, 4.70. Molecular weight for **17**: calcd, 985; found (osmometric), 1020 ± 100. UV/vis (CH_2Cl_2): λ_{max} (log ϵ) 243 (sh, 4.62), 249 (4.61), 255 (4.66), 262 (4.55), 277 (4.35), 388 (4.54), ca. 475 (sh, 3.55) nm. IR (THF): 1952 (vs), 1969 (m, sh). IR (mineral oil mull): 2030 (vw), 1970 (w), 1943 (vs), ca. 1920 (sh), 1300 (w), 1163 (m), 1093 (w), 1034 (w), 1020 (w, br), 890 (w), 800 (w), 740 (sh), 692 (w) cm^{-1}. Far-IR (mineral oil mull): 560 (sh), 538 (m), 512 (w), 423 (w) cm^{-1}.

The combined benzene-insoluble materials were dissolved in ca. 5 mL of THF and precipitated from solution with petroleum ether, yielding 0.12 g (36%) of a dark brown solid after cooling to −40 °C; mp 170 °C dec. Anal. Calcd for $C_{46}H_{44}P_2Si_2FeCo_2O_6$: C, 56.11; H, 4.50. Found: C, 55.52; H, 4.81. Molecular weight for **17**: calcd, 985; found (osmometric), 1180 ± 100. IR (THF): 1952 (vs), 1969 (m, sh).

Oxidation of 12. Air was bubbled through a solution of 40 mg of **12** (benzene-insoluble form) in 0.5 mL of chloroform for 30 min. The brown color was rapidly discharged, and a green precipitate appeared. Removal of solvent from the filtered solution left **2**-dioxide as an orange solid. (For spectral data, see Tables I and III.)

Reaction of 12 with KH. A solution of 35 mg (0.03 mmol) of **12** in 5 mL of THF was treated with ca. 3.5 mg (0.08 mmol) of KH. After 4 h of stirring, the original deep brown-red color had changed to an olive green, and a small quantity of green precipitate had appeared. The supernatant displayed IR bands at 1816 (m, sh), 1844 (vs), 1890 (w), and 1924 (s) cm^{-1}. Addition of 73 mg (0.13 mmol) of bis(triphenylphosphine)iminium chloride followed by stirring for 12 h and decantation gave rise to a solution of the PPN salt of dianion **14** having IR absorptions at 1835 (vs), 1883 (s), and 1921 (s) cm^{-1} (the band at 1883 cm^{-1} is due to $PPN^+Co(CO)_4^-$).[18]

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Contribution from the Department of Chemistry and the Program in Biochemistry and Biophysics,
Washington State University, Pullman, Washington 99164

Synthesis and Characterization of Cobalt(III) Ethylenediamine-*N*,*N*′-diacetate Complexes with Azo Dyes and Azo Amino Acids

KOZO IGI, MICKEY S. URDEA, and J. IVAN LEGG*

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A series of ternary cobalt(III) complexes containing the quadridentate ligand ethylenediamine-*N*,*N*′-diacetate (EDDA) and bidentate azo ligands have been prepared and characterized as models for cobalt(III) azo protein derivatives. The azo ligands investigated are an azo naphthol dye, *p*-(2-hydroxy-1-naphthylazo)benzenesulfonic acid (OD-II = orange dye II), an azo phenol dye, 2-(4-carboxyphenylazo)-4,5-dimethylphenol (CDP), and azo amino acid derivatives, *N*-acetyl-3-(arsanilazo)-L-tyrosine (NA-MAT), *N*-acetyl-2-(arsanilazo)-L-histidine (NA-MAH(C-2)), *N*-acetyl-4-(arsanilazo)-L-histidine (NA-MAH(C-4)), and *N*-acetyl-2,4-bis(arsanilazo)-L-histidine (NA-BAH), which are direct analogues of the cobalt(III) azo protein derivatives. Two of the possible geometrical isomers for the OD-II and CDP complexes were separated and characterized by their ^{1}H NMR spectra. The visible electronic absorption spectra of the azo dyes and azo amino acids are distinctly and systematically altered upon cobalt(III) coordination, permitting the quantitative determination of cobalt(III) complexation to azo proteins. The absorption spectra vary little between isomers.

Introduction

We have developed a method for the complexation of substitution-inert Co(III) to histidine and tyrosine residues in proteins.[1-3] In order to direct and stabilize Co(III) coordination, we converted histidine or tyrosine residues to an azo histidine or azo tyrosine by diazo coupling with an aryl diazonium salt such as diazotized arsanilic acid. The chromophoric azo amino acids serve as bidentate chelating agents and are preferential sites for cobalt complexation in the proteins investigated. Substitution-labile Co(II) is introduced to the azo protein as the diaquo ethylenediamine-*N*,*N*′-diacetate (EDDA)[4] complex and is subsequently oxidized in situ to produce the exchange-inert Co^{III}(EDDA)(azo protein) complex. The octahedral, six-coordinate Co(III) complex is linked to the protein only through the bidentate azo amino acid. The resulting Co(III)–azo protein complexes are very stable to ligand exchange.[1-3]

This method has been employed to specifically label tyrosine 248 of carboxypeptidase A and constitutes the first modification of the enzyme which blocks only the phenolic oxygen of this active site residue.[1] This modification has provided information as to the potential role of tyrosine 248 in the hydrolysis of peptides and esters.[5] The Co(III) can be reduced with Fe^{II}EDTA, resulting in full return of the original azo protein properties. With the use of this technique, a radiolabeled derivative of insulin has been produced with ^{57}Co and employed in a radioimmunoassay.[3]

Successful production and characterization of the Co(III) azo protein derivatives is dependent on the synthesis and full characterization of Co(III) model complexes. Initial studies employed terdentate azo tyrosine analogues[6] and bidentate azo tyrosine analogues[7] as they relate more specifically to the Co(III) derivative of arsanilazotyrosine-248 carboxypeptidase.[1] The work presented here describes the preparation, isomer separation, and characterization of the OD-II and CDP[4] complexes of Co^{III}EDDA and the preparation and characterization of the Co^{III}(EDDA)(azo tyrosine and histidine) complexes which are direct analogues of the azo protein derivatives currently under investigation.[1-3] It is shown that distinct changes occur in the visible spectrum of the azo dyes or azo amino acids upon Co(III) coordination which are generally useful in determining the extent and specificity of Co(III) complexation to azo proteins. Importantly, it has been shown that the coordination modes of these ligands have little effect on the absorption spectrum. Thus it is not necessary to define the stereochemistry of the Co(III) complex in order to characterize a modified protein. The determination of cobalt coordination to the azo chromophores by spectral analysis is far more sensitive than in the absence of chromo-

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*To whom correspondence should be addressed at the Department of Chemistry.

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(4) Abbreviations used are as follows: EDDA, ethylenediamine-*N*,*N*′-diacetic acid; OD-II, orange dye II, *p*-(2-hydroxy-1-naphthylazo)benzenesulfonic acid; CDP, 2-(4-carboxyphenylazo)-4,5-dimethylphenol; NA-MAH(C-2), *N*-acetyl-2-(arsanilazo)-L-histidine; NA-MAH(C-4), *N*-acetyl-4-(arsanilazo)-L-histidine; NA-BAH, *N*-acetyl-2,4-bis(arsanilazo)-L-histidine; NA-MAT, *N*-acetyl-3-(arsanilazo)-L-tyrosine; ISTEA, distilled 2-propanol and triethylamine bicarbonate buffer, pH 9.5.

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