Other observed infrared spectral peaks for these polymers were as follows (cm^{-1}). $(CF_3)_2PCN$ product: 2043 (m), 1995 (m), 1137 (br, poorly resolved), 726 (m, br), 620 (vw). $CF_3P(CN)_2$ product: 2047 (m), 1995 (m), 1135 (s, br), 725 (m, br), 621 (w).

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Diamagnetic Anisotropy Induced by Metal–Metal Multiple Bonds[1a]

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The most compelling criterion for the existence of a metal–metal bond has been, and remains, the metal–metal bond distance as determined by crystallographic techniques. Recently metal–metal double,[2] triple,[3,4] and quadruple[4] bonds have been proposed to exist in a number of compounds. These proposals have been based primarily on the exceptionally short metal–metal distances in these compounds. Undoubtedly, the length of a bond of a given multiplicity between a given pair of metal atoms is a sensitive function of a variety of parameters, including oxidation states, nature of additional ligands, and other aspects of molecular structure. It is apparent, therefore, that the use of interatomic distances to infer the multiplicity of metal–metal bonds requires caution. Indeed, the question of whether a multiple metal–metal bond actually exists rests squarely on the interpretation of metal–metal bond distances, the precise validity of which remains unclear.

Our interest in the general area of metal–metal bonds has prompted us to examine the question of multiplicity in such systems. Here we wish to report the results of an investigation that uses a noncrystallographic technique for probing the presence of certain multiple metal–metal centers.

Experimental Section

General.—All solvents were spectro quality and were degassed prior to use. Phosphine and phosphites were purchased from Strem Chemicals and used without further purification. Nmr samples were prepared and sealed under nitrogen. Nmr spectra were determined on a Varian HA-100 spectrometer. Optical spectra were recorded on sealed samples using a Cary Model 14 spectrophotometer. The infrared spectra of all new complexes were determined as chloroform solutions in sealed sodium chloride cells on a Perkin-Elmer Model 337 grating spectrophotometer and were essentially equivalent to the spectrum observed for the uncomplexed ligand. Analyses and molecular weights were determined in the microanalytical laboratories of Stanford University and Galbraith Laboratories, Knoxville, Tenn.

Hexachlorobis(triethylphosphine)dirhenium(III), $Re_2Cl_6[P(C_2H_5)_3]_2$, was prepared by the procedure of Cotton and Foxman.[5] ***trans*-Dichlorobis(tri-*n*-butylphosphine)platinum(II)** was prepared by the procedure of Grim, *et al.*[6]

Preparation of Dinuclear Rhenium(III) Complexes.—The procedure outlined below for the preparation of hexachlorobis(tri-*n*-butylphosphine)dirhenium(III) is typical of the general method used.

Tetra-*n*-butylammonium octachlorodirhenium,[7] $[Re_2Cl_8][N(C_4H_9)_4]_2$ (1.0 g, 0.88 mmol), was suspended in 25 ml of methanol containing 1 ml of concentrated hydrochloric acid and tri-*n*-propylphosphine (1.0 g, 6.2 mmol) was added. The solution turned green immediately. After stirring for an additional 30 min, the solution was chilled to −20° and the green crystals collected by suction filtration. The isolated yield was 93%.

Preparation of Dinuclear Molybdenum(II) Complexes.—A typical procedure used to prepare the desired dinuclear molybdenum(II) complexes is presented below.

Tetrachlorotetrakis(triethylphosphine)dimolybdenum(II), $Mo_2Cl_4[P(C_2H_5)_3]_4$.—Pentaammonium nonachlorodimolybdenum(II) monohydrate,[8] $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ (2.0 g, 3.2 mmol), was placed in a 40-ml centrifuge tube containing a Teflon-coated stirrer bar. The tube was capped with a rubber septum stopper and flushed with prepurified nitrogen. Oxygen-free methanol (30 ml) was added, followed by 2.0 g (17 mmol) of triethylphosphine. The solution turned blue immediately. The resulting mixture was stirred for 1 hr, chilled to −78°, and centrifuged. The supernatant solution was removed through a cannula employing a positive pressure of nitrogen. Fresh oxygen-free methanol was again added and the tube was shaken, cooled, and again centrifuged. The solid was washed a total of five times. The remaining solid was suspended in 20 ml of oxygen-free methanol, chilled to −78°, and then filtered under a positive pressure of nitrogen. The isolated solid was obtained in 85% yield. Tetrachlorotetrakis(triethylphosphine)dimolybdenum(II) is stable indefinitely at ambient temperatures in the absence of oxygen; it is oxidized slowly on exposure to room atmosphere, but solutions decompose rapidly in presence of oxygen.

Results and Discussion

It has been recognized for some time that the anomalous shielding observed in the ^1H nmr spectra of certain organic compounds which contain a hydrogen nucleus in the vicinity of a carbon–carbon multiple bond is a direct consequence of the diamagnetic anisotropy that results when the circulating electrons within this multiple bond are subjected to an external field. The theoretical aspects of such long range shielding have been treated by McConnell,[9] the approximate relationship for an axially symmetrical group of electrons being

$$\sigma_{av} = \frac{(3\cos^2\theta - 1)(X_L - X_T)}{3r^3}$$

where r is the distance between the proton and the electrical center of gravity of the multiple bond, θ is the acute angle between r and the symmetry axis, and X_L and X_T are respectively the longitudal and transverse magnetic susceptibilities of the bond in question. The subscript "av" is included to indicate that the shielding, σ, has been averaged over all orientations of the system. From the angular dependence of this relationship it is noted that the value of the function

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TABLE I
ANALYTICAL DATA FOR $Re_2Cl_6L_2$ AND $Mo_2Cl_4L_4$

Compound	Formula	Mol wt[a]		C, %		H, %		Cl, %	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Re_2Cl_6[P(C_3H_7)_3]_2$	$C_{18}H_{24}Cl_6P_2Re_2$			23.86	23.89	4.64	4.10	23.53	23.42
$Re_2Cl_6[P(C_4H_9)_3]_2$	$C_{24}H_{54}Cl_6P_2Re_2$	989	980	28.82	28.91	5.40	5.26	21.32	21.63
$Mo_2Cl_4[P(C_2H_5)_3]_4$	$C_{24}H_{60}Cl_4Mo_2P_4$	806	793	35.75	35.60	7.44	7.41	17.61	17.55
$Mo_2Cl_4[P(C_3H_7)_3]_4$	$C_{36}H_{84}Cl_4Mo_2P_4$	974	967	44.35	44.33	8.62	8.60	14.58	14.28
$Mo_2Cl_4[P(C_4H_9)_3]_4$	$C_{48}H_{108}Cl_4Mo_2P_4$	1142	1149	50.43	50.23	9.46	9.24	12.43	12.24
$Mo_2Cl_4[P(C_6H_5)(CH_3)_2]_4$	$C_{32}H_{44}Cl_4Mo_2P_4$	886	867	43.34	43.55	4.97	4.76	16.03	16.03
$Mo_2Cl_4[P(OCH_3)_3]_4$	$C_{12}H_{36}Cl_4Mo_2O_{12}P_4$	833	810	17.28	17.07	4.32	4.28	17.04	17.00

[a] Osmometrically, $CHCl_3$.

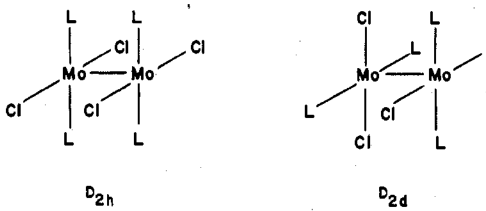

Figure1.—Suggested idealized structures for the dinuclear complexes $Mo_2Cl_4L_4$.

changes sign at 55° 44′ so that an axially symmetrical bond can either shield or deshield a neighboring proton depending on their relative orientations. The sign of the shielding is also seen to be further dependent on the value of the difference ($X_L - X_T$) while the magnitude of the shielding increases toward the symmetry axis and toward the electrical center of gravity.

These considerations, taken together with the fact that an accurate structure determination has demonstrated the close proximity of the ligand α-methylene protons to the metal–metal center in the dinuclear complex $Re_2Cl_6[P(C_2H_5)_3]_2$,[5] suggested to us that it would not be unreasonable to expect the ^1H nmr spectra of these complexes might reflect an anomalous shielding of ligand protons if the multiple metal–metal centers which have been proposed actually existed. With this purpose in mind we prepared and examined the ^1H and ^{31}P nmr spectra of a number of phosphine and phosphite complexes of dinuclear rhenium(III) and molybdenum(II).

The desired complexes of dinuclear rhenium(III) were either known or synthesized using a procedure similar to that developed by Cotton and coworkers.[5] The phosphine and phosphite complexes of dinuclear molybdenum(II) were unknown. These compounds were prepared by reaction of pentaammonium nonachlorodimolybdenum monohydrate, $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, with the appropriate ligand. The spectral, analytical, and molecular weight data for these compounds leave no doubt that they are in fact complexes of the general formulation $Mo_2Cl_4L_4$. In view of the demonstrated isostructural nature of dinuclear molybdenum(II) and dinuclear rhenium(III) compounds[4d] and the considerable similarity between the spectral properties of these new compounds (*vide infra*) and those of known dinuclear rhenium(III) compounds, it is reasonable to suggest that these new molybdenum complexes contain the metal–metal bonded Mo_2 unit, each metal center of which is coordinated by a square set of four ligands as depicted in Figure 1. As demanded by their nmr data, the only structures that are reasonable for these compounds, given the above considerations, are those in which two phosphine ligands are coordinated to the same metal center in a trans configuration.

Nmr Spectra.—The chemical shifts of protons on the alkyl groups in organophosphorus compounds depend to a considerable extent on the proximity of these protons to the hetero center and on the electron density at the phosphorus atom as determined by the groups that are substituted on it.[10,11] Thus, for example, quaternization of triethylphosphine leads to a sufficient chemical shift difference between methylene and methyl protons that an essentially first-order pattern is obtained.[11] It follows, therefore, that relative to the uncoordinated ligand, the protons of a tertiary alkylphosphine which is coordinated to an electropositive metal center are likely to suffer some deshielding. The effect, as shown for several examples in Table II, is usually small.

TABLE II
^1H AND ^{31}P CHEMICAL SHIFTS FOR TRI-*n*-BUTYLPHOSPHINE AND SOME RELATED DERIVATIVES

$$P\text{–}\overset{\alpha}{CH_2}\text{–}\overset{\beta}{CH_2}\text{–}\overset{\gamma}{CH_2}\text{–}\overset{\epsilon}{CH_3}$$

Solute		^1H $\delta^{a,c}$ (J)	^{31}P δ^b (J)
$P(C_4H_9)_3$	α β γ	1.39	33
	ϵ	0.92 t ($J_{CH_3-CH_2} = 6.5$)	
$[ICu \cdot P(C_4H_9)_3]_4$	α β γ	1.50–1.63 br, m	34 br
	ϵ	0.92 t ($J_{CH_3-CH_2} = 6.0$)	
$[IAg \cdot P(C_4H_9)_3]_4$	α β γ	1.58–1.65 br, m	19 br
	ϵ	0.97 t ($J_{CH_3-CH_2} = 6.5$)	
trans-$Cl_2Pt[P(C_4H_9)_3]_2$	α β γ	1.56–1.68 br, m	-5^d
	ϵ	0.99 t ($J_{CH_3-CH_2} = 6.0$)	
$[(C_4H_9)_4P]I$	α	2.56 br	-32^e
	β γ	1.63 br, m	
	ϵ	1.04 t ($J_{CH_3-CH_2} \approx 6$)	

[a] ^1H spectra were recorded at 100 MHz using ~0.5 *M* solutions in $CDCl_3$. Chemical shifts (δ) are in parts per million downfield from internal TMS; coupling constants (J) are in hertz. Notation: br = broad, t = triplet, and m = multiplet. [b] Spectra were taken at 40.5 MHz using ~1 *M* solutions in $CDCl_3$. Chemical shifts are in parts per million relative to external 85% H_3PO_4. [c] Individual chemical shift assignments were not made to groups of protons indicated by braces. [d] J. F. Nixon and A. Pidcock, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **2**, 345 (1969). [e] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 227 (1967).

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TABLE III

^{1}H CHEMICAL SHIFTS (δ) FOR L, $Re_2Cl_6L_2$, AND $Mo_2Cl_4L_4$[a]

$P{-}\overset{\alpha}{CH_2}{-}\overset{\beta}{CH_2}{-}\overset{\gamma}{CH_2}{-}\overset{\epsilon}{CH_2}$

Solute	δ^b	L = $P(C_2H_5)_3$	$P(n\text{-}C_3H_7)_3$	$P(n\text{-}C_4H_9)_3$	$P(C_6H_5)(CH_3)_2$	$P(OCH_3)_3$	$P(C_6H_5)_3$
L							
	α }	~1.2[c]	} 1.40 br	} 1.39 br	1.39[d]	3.50[d]	
	β }						
	γ		1.02 t				
	ϵ			0.92 t			
	Aryl				7.29		7.35
		$J_{CH_3-CH_2}$ = 7.6[c] J_{CH_3-P} = 13.7[c] J_{CH_2-P} = 0.5[c]	$J_{CH_3-CH_2}$ = 6.4	$J_{CH_3-CH_2}$ = 6.5	J_{CH_3-P} = 2.0	J_{CH_3-P} = 11.0	
$Re_2Cl_6L_2$							
	α	2.44 m	2.31 br, m	2.38 br	1.30		
	β	1.48 m	1.50 br, m	} 1.39 br			
	γ		0.95 t				
	ϵ			0.95 t			
	Aryl				7.30		*d*
		$J_{CH_3-CH_2}$ = 8.5 J_{CH_3-P} = 16.5 J_{CH_2-P} = 9.0	$J_{CH_3-CH_2}$ = 7.5	$J_{CH_3-CH_2}$ = 6.5	J_{CH_3-P} = 13.5		
$Mo_2Cl_4L_4$							
	α	2.18 m	2.15 br, m	2.18 br	1.82[e]	3.75[e]	
	β	1.08 m	1.52 br, m	} 1.34 br			
	γ		0.97 t				
	ϵ			0.92 t			
	Aryl				7.10		7.40
		$J_{CH_3-CH_2}$ = 8.0 J_{CH_3-P} = 10.0 J_{CH_2-P} = 8.5	$J_{CH_3-CH_2}$ = 7.5	$J_{CH_3-CH_2}$ = 6.0			

[a] Spectra were taken at 100 MHz using ~0.5 solutions in $CDCl_3$. Chemical shifts (δ) are in parts per million downfield from internal TMS; coupling constants (J) are in hertz. Notation: br = broad, t = triplet, and m = multiplet. [b] Individual chemical-shift assignments were not made to groups of protons indicated by braces. [c] For an analysis of the triethylphosphine (A_3B_2X) system see, P. T. Narashiman and M. T. Rogers, *J. Chem. Phys.*, **34,** 1049 (1961). [d] Spectra could not be obtained because of the limited solubility of this substance. [e] Apparent triplet.

The ^{1}H nmr spectra of $Re_2Cl_6[P(n\text{-}C_4H_9)_3]_2$ and $Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$ are shown in Figure 2. For comparison the spectra of *trans*-bis[tri-*n*-butylphosphine]-platinum(II) chloride, tetrakis[iodo(tri-*n*-butylphosphine)silver(I)], and uncomplexed tri-*n*-butylphosphine are also shown. Consonant with our expectation, these spectra reveal that certain ligand protons in these dinuclear complexes *do* suffer a substantial deshielding.

To exclude the possibility that the observed deshielding was the result of second-order paramagnetism,[12] these spectra were examined over a temperature range of −100 to +150°. The chemical shifts of all protons showed only those small changes usually associated with temperature changes of this magnitude. Thus, second-order paramagnetism cannot be responsible for the considerable chemical shift differences observed.[13]

The ^{1}H chemical shifts of various phosphine and phosphite complexes of dinuclear rhenium(III) and dinuclear molybdenum(II) are given in Table III. These data confirm the generality of the initial observation. Table IV lists the ^{31}P chemical shifts for these same complexes.

There are several additional features of the data in Tables III and IV that are noteworthy. First, barring accidental magnetic equivalence, these data require that all the phosphorus nuclei in any given complex are, on the average, in magnetically equivalent environments. Second, a trans orientation of phosphorus centers about each molybdenum atom is suggested by the fact that the methyl resonance for both $Mo_2Cl_4[P(OCH_3)_3]_4$ and $Mo_2Cl_4[P(C_6H_5)(CH_3)_2]_4$ appears as an apparent triplet.[14] The failure to observe a similar pattern in the spectrum of $Re_2Cl_6[P(C_6H_5)(CH_3)_2]_2$ suggests that there is little or no coupling between trans oriented ligands coordinated to adjacent metal centers. These observations, when taken together with the molecular weight data for the newly prepared molybdenum complexes, strongly support the dinuclear structures suggested in Figure 1.

Finally, the downfield methylene resonance observed for the tri-*n*-butylphosphine complexes exhibited notice-

TABLE IV

^{31}P CHEMICAL SHIFTS FOR L, $Re_2Cl_6L_2$, AND $Mo_2Cl_4L_4$[a]

Solute	δ	Solute	δ
$P(C_2H_5)_3$	20	$Mo_2Cl_4[P(C_2H_5)_3]_4$	−12
$P(C_3H_7)_3$	33	$Mo_2Cl_4[P(C_3H_7)_3]_4$	−7
$P(C_4H_9)_3$	33	$Mo_2Cl_4[P(C_4H_9)_3]_4$	−7
$P(OCH_3)_3$	−144	$Mo_2Cl_4[P(OCH_3)_3]_4$	−133
		$Re_2Cl_6[P(C_4H_9)_3]_2$	−10

[a] Spectra were taken at 40.5 MHz using ~1 *M* solutions in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to external 85% H_3PO_4.

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(12) The possibility of second-order paramagnetism in dirhenium complexes has been suggested: F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4,** 326 (1965).

(13) The considerable effect which temperature has on the chemical shift of ligands coordinated to metals, including Re(III), which display second-order paramagnetism has been investigated: E. W. Randall and D. Shaw, *J. Chem. Soc. A*, 2867 (1969).

(14) The virtual coupling between chemically equivalent trans oriented phosphorus nuclei and its utility as a stereochemical probe is well documented: R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42,** 2282 (1964); J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963); *J. Chem. Soc. A*, 770 (1966); T. H. Siddall and W. E. Stewart, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5,** 33 (1969), and references therein.

able broadening (*cf.* Figure 2). At ambient temperatures, the peak width at half-height was ~20 Hz. The magnetic field invariance of signal shape and line width indicate that the protons in these methylenes have the same chemical shift. It was further observed that spectra of samples cooled to −80° or heated to +150° displayed no appreciable difference in line shape or signal width, nor did the line shape or peak width exhibit any significant dependence on solvent viscosity. Sequential addition of free tri-*n*-butylphosphine to solutions of these complexes produced no noticeable change in the appearance of the α-methylene signal. Respectively, these observations suggest that the line broadening is *not* the result of (1) restricted rotational conformations,[15] (2) spin–spin coupling between these protons and the naturally occurring isotopes of molybdenum -95 (15%, $S = {}^5/_2$), -97 (10%, $S = {}^5/_2$), and rhenium -185 (37%, $S = {}^5/_2$), -187 (63%, $S = {}^5/_2$),[16] or (3) exchange broadening resulting from chemical exchange such has recently been observed in certain "virtually coupled" metal–phosphine complexes.[17]

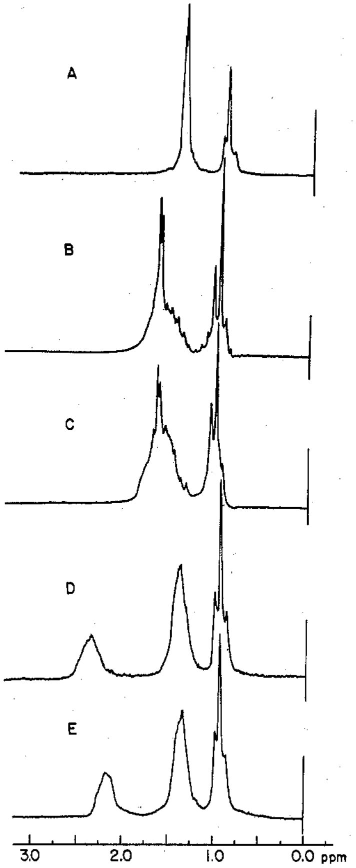

Figure 2.—Nmr spectra (100 MHz, $CDCl_3$): A, tri-*n*-butylphosphine; B, tetrakis[iodo(tri-*n*-butylphosphine)silver(I)], $[IAg\cdot P(C_4H_9)_3]_4$; C, *trans*-dichlorobis(tri-*n*-butylphosphine)platinum(II), $PtCl_2[P(C_4H_9)_3]_2$; D, hexachlorobis(tri-*n*-butylphosphine)dirhenium(III), $Re_2Cl_6[P(C_4H_9)_3]_2$; E, tetrachlorotetrakis(tri-*n*-butylphosphine)dimolybdenum(II), $Mo_2Cl_4[P(C_4H_9)_3]_4$.

Such line broadening is most likely a consequence of the fact that these resonances are each composed of many closely spaced lines as a result of extensive proton–proton coupling. Where such coupling is decreased, as it is for example in the tri-*n*-propylphosphine complex, considerable fine structure is observed in these resonances. Not unexpectedly, therefore, the ^1H spectrum of the triethylphosphine complex is observed to be essentially first order.

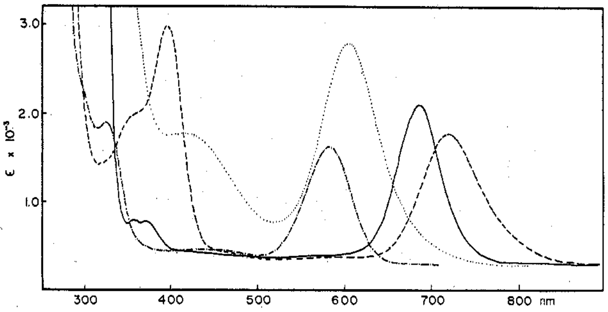

Figure 3.—The electronic abosrption spectra of some dinuclear rhenium(III) and molybdenum(II) compounds in methylene chloride: ——, $[Re_2Cl_8][N(C_4H_9)_4]_2$; ----, $Re_2Cl_6[P(C_4H_9)_3]_2$; -·-·-·-·-, $Mo_2Cl_4[P(C_4H_9)_3]_4$; ......, $Mo_2Cl_4[P(OCH_3)_3]_4$.

Electronic Absorption Spectra.—Cotton has examined the electronic spectra of a series of dirhenium complexes and given a partial assignment of them in terms of a simple bonding scheme.[18,19] On this basis the characteristic absorption of the octahalo species $Re_2X_8^{2-}$ between 600 and 800 nm was assigned to a transition from the δ-bonding orbital to one of the nonbonding σ orbitals.

The electronic spectra of several related dinuclear complexes of rhenium(III) and molybdenum(II) are presented in Figure 3. The characteristic visible absorption observed in the dinuclear rhenium complexes is shifted to higher energies in the molybdenum complexes. Assuming these absorptions are similar in origin, such a shift is consistent with the decrease in separation of ground and excited states expected to occur in proceeding from second- to third-row metal complexes of similar molecular orbital arrangement.

In conclusion, it is worthwhile making explicit that as a technique for probing the presence of multiple metal–metal centers, it is apparent that the successful application of diamagnetic anisotropic induced chemical shifts requires that the system under investigation conform to rather rigid geometrical considerations. Moreover, such shielding can only be so interpreted in the absence of additional functionalities (*e.g.*, carbonyl and arene systems) capable of inducing a similar effect, while the failure to observe such long-range shielding does not, of course, negate the presence of a multiple metal–metal center.

Acknowledgments.—The author is indebted to Professor James P. Collman (Stanford University) for his considerable generosity and aid and wishes to thank Dr. Dorothy Z. Denney (Rutgers University) for extensive assistance in obtaining nmr spectra.

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