

by extended Hückel calculations. However, the magnetic orbitals in the top and bottom faces of the cubane are delocalized toward the bridging oxygen atom to a much lesser degree than the d_{xy} orbitals in the dimers^{22,23} treated by Kahn and co-workers. This being the case, the bending of the pseudodimer in the present complex should have a smaller effect on the ferromagnetic interaction than the bending in the bis(μ -oxo)-bridged dimers.

The side faces of the cubane display all three different Cu-O-Cu bond lengths. The two unequal Cu-O-Cu angles in these faces are 95.0 (2) and 103.7 (2)° with the mean value being 99.4°. The exchange interaction within the side faces of the cubane subcore is clearly antiferromagnetic. The overlaps, in the side faces of the cubane, of the d_{z^2} magnetic orbitals on the copper atoms with the orbitals on the bridging oxygen atoms form interaction pathways that lead to the observed moderate antiferromagnetic interaction. There are contributions to the observed J value from both Cu-O-Cu pathways, and it is clear that the contribution involving the large Cu-O-Cu angle of 103.7 (2)°, which is ex-

pected to be antiferromagnetic, dominates the contribution from the 95.0 (2)° Cu-O-Cu pathway. This latter angle is very close the ground-state inversion angle of 95.7° in bis(μ -alkoxo)-bridged copper(II) dimers, and only a small positive value of J would have been expected for it.

This work has opened up two important new avenues of research. First, it is important that additional members of this new structural class of aminoalcohol complexes be prepared and characterized so that the nature of the superexchange interactions and pathways may be understood more clearly. Secondly, and perhaps more importantly, the question of capping additional faces now arises. These two problems will guide our research in this area.

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Registry No. $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8](\text{ClO}_4)_4$, 100113-85-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic temperature factor coefficients for non-hydrogen atoms (Table SI), and fractional coordinates for hydrogen atoms (Table SII) (13 pages). Ordering information is given on any current masthead page.

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A Structural Analysis of the Semibridging Carbonyl

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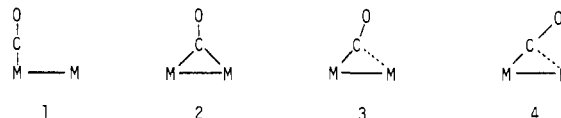
The structural data for terminal, linear and bent semibridging, and symmetrically bridging CO groups in 47 compounds are subjected to a detailed quantitative analysis. As first suggested by Cotton, the terminal, bent semibridging, and symmetrical bridging systems form a smooth structural continuum that can be identified with the terminal-bridge-terminal CO-exchange reaction trajectory. The linear semibridging carbonyls can be divided into three major types on structural and chemical grounds. Type I contains strongly interacting systems, with one linear semibridging CO per dimetal unit. Type II, with more than one such CO bridge and multiple M-M bonding, shows less interaction. Type III systems, containing a transition metal and either Au or a main-group metal have, it is proposed, no significant interaction between the second metal and the ostensibly bridging CO. Type IV is as yet only tentatively formulated as it contains but a single example: $\text{Mn}_2(\text{CO})_5(\text{dppm})_2$. The current bonding models are discussed with reference to these data, and their validity for the different structural types is considered.

A fascinating aspect of structural organometallic and coordination chemistry is the high structural variability that can be observed in such groups as $\text{M}(\mu\text{-CO})\text{M}$, $\text{M}(\mu\text{-H})\text{M}$, and $\text{C}(\mu\text{-H})\text{M}$. The closest analogy outside organometallic chemistry is probably the hydrogen bond. In each case the interactions involved must be much weaker than the full covalent bonds normally encountered in structural chemistry. This variability allows us to learn something about the types of potential energy surfaces associated with these interactions.

This paper attempts to show how a detailed structural analysis of an inorganic functional group can provide useful information in two respects. First, it can help identify and characterize different structural types and test rival theoretical pictures of bonding. Second, it can, as emphasized by Bürgi and Dunitz¹ for organic systems, give information about reaction trajectories. Our earlier work in this area² involved the C-H...M bridge,³ from which we were able to suggest a detailed reaction trajectory for $\text{M} + \text{C-H} \rightarrow \text{C-M-H}$. From these results we were able not only to confirm the main features of the C-H...M bonding but also to gain a deeper understanding of the factors that determine whether a metal complex will react with an alkane C-H bond (alkane activation) or with a ligand C-H bond (cyclometalation). We concluded that sterically uncongested systems would favor the alkane reaction.

We were also able to understand the observed selectivity for attack at unhindered alkane C-H bonds. The success of this work led us to ask whether the same method might also throw light on other organometallic problems.

This paper reports our results on CO, a ligand that occupies a place of central importance in organometallic chemistry. We were attracted to this group because it adopts a number of distinct structural forms in its complexes: terminal (1), symmetrically bridging (2), and semibridging (both bent (3) and linear (4) forms



have been identified). In the case of 4, the unusual linear semibridging form, rival views of the bonding description have been proposed and we hope to throw some light on this problem.

The bent semibridging carbonyl is closely associated with the important work of Cotton.^{4a} He proposed that semibridging CO groups could be thought of as constituting a structural continuum that leads from the terminal to symmetrical bridging arrangements and that they represent "stopped-action views" (i.e. a kinetic

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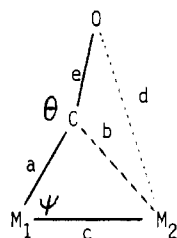


Figure 1. Definitions of the structural parameters studied.

pathway) for this process. We have given quantitative form to this proposal and have used the resulting trajectory as a benchmark for the study of the rarer linear semibridging carbonyl. Other useful reviews^{4b} of the whole area are also available.

In an important previous study of the linear case, Curtis^{4b} plotted the M_1-C-O angle θ (see Figure 1) against his bond asymmetry parameter $[(M_1-C) - (M_2-C)]/(M_1-C)$ and showed that bent and linear semibridging carbonyls followed two different curves. For the bent systems, θ falls steadily from 180 to about 140° as the M_1-C and M_2-C distances become more similar, but in the linear cases, θ does not fall below 170° even when the M_2-C bond is almost as short as in the bent case.

Rather than set out with a precise definition of the different types of bridging carbonyl, we have gathered data from a variety of structures in the hope that the results would tell us what types of CO we were really justified in distinguishing. We will first report a study of cases 1-3, together with the corresponding reaction trajectory for terminal-bridging-terminal CO fluxionality between two metal atoms in a cluster. We then will turn to the linear semibridging carbonyl. Our results suggest that the situation is more complicated than was previously believed: three major and one minor type of linear semibridging carbonyl are identified, and the most appropriate bonding description for each is suggested.

Results and Discussion

The Bent Semibridging Carbonyl. We studied the literature to find examples of bridging, semibridging, and terminal carbonyls in binuclear complexes and clusters (Table I). To maintain the

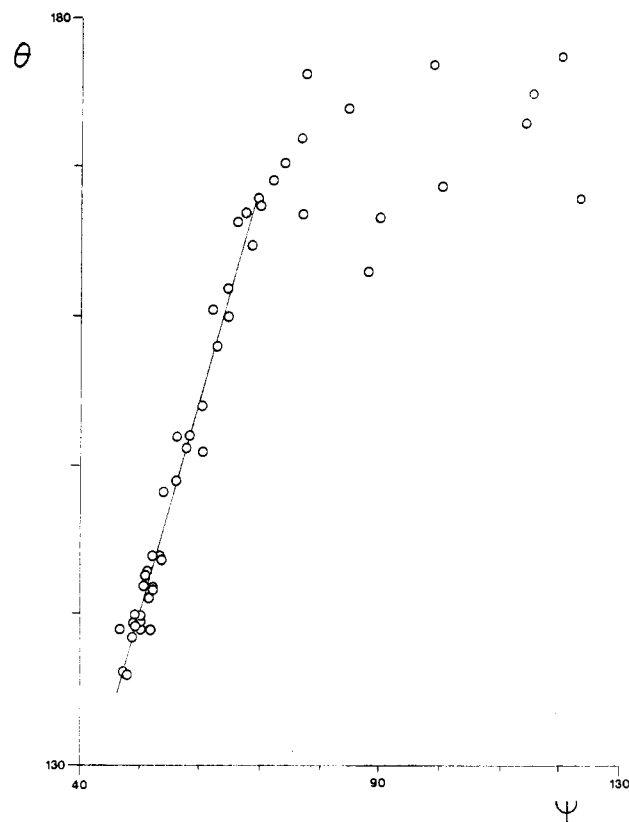


Figure 2. θ vs. ψ for the bent semibridging, bridging, and terminal carbonyls.

greatest degree of comparability, iron compounds were preferred, and we only moved to other metals when suitable data were not

- (5) (a) We did not adjust the angles for covalent-radius differences because the angular adjustments turn out to be small. (b) A slight error is involved in using this expression in cases where M_1 and M_2 have a covalent radius that differs substantially from that of iron, but the correction is small.
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Table I. Data for the Compounds Studied^a

compd	a	b	e	ψ	θ	type	ref	compd	a	b	e	ψ	θ	type	ref	
Fe(CO) ₁₁ PPh ₃	1.9	1.99		50	139	bsb	11	Fe ₂ Cp ₂ (CO) ₄	1.908	1.918		48.75	139.4	b	31	
	1.86	2.04		52	144				1.917	1.925		48.93	139.2			
	1.86	2.07		53	144				1.902	1.902		48.51	138.5	b	32	
	1.85	2.04		52	142				[Cp ₂ Fe ₂ (CO) ₃ (CHMe) [Cp ₂ Fe ₂ (CO) ₃ (SEt)] ⁺	1.95	1.96		48.88	140.0	b	33
	1.65	3.45		108	172	t			Cp ₂ Fe ₂ (CO) ₃ (GeMe ₂)	1.902	1.923		46.94	136.2	b	34
Fe ₄ (CO) ₁₃ ²⁻	1.71	3.62		114	173			Cp ₂ Fe ₂ (CO) ₃ (CSEt)	1.923	1.949		50.04		b	35	
	1.85	2.33		62.7	158	bsb	12	Cp ₂ Fe ₂ (CO) ₃ - (C ₂ CN) ₂	1.91	1.97		50.76	143.0			
	1.81	2.28		61.4	155			(C ₆ H ₄ Me ₄)Fe ₂ (CO) ₅	1.91	1.97		46.31	139.0	b	37	
	1.8	2.24		60.2	151			(GePh ₂)Fe ₂ (CO) ₉	1.98	2.08		50.60	142.7	b	38	
	1.81	3.42		100.3	168.8	t		Mo ₂ (O- <i>t</i> -Bu) ₆ (CO)	1.892	1.892		51.9	141.8	b	39	
	1.75	3.33		98.7	176.9			CpCo(CO) ₂ ZrCp ₂	1.699	1.992	1.200	50.8	176.7	lsb-I	40	
	1.69	2.76		77.3	176.3			CpMo(CO) ₂ (MeCO)ZrCp	1.746	2.063	1.241	43.99	172.3	lsb-I	41	
	1.66	2.74		76.7	166.9			CpMo(CO) ₂ NbCp ₂	1.81	2.05	1.22	46.03	171.01	lsb-I	42	
	1.66	3.63		120.3	177.5			CpW(CO) ₂ (C- <i>tolyl</i>)TiCp ₂	1.77	2.05	1.21	47.5	165.0	lsb-I	43	
	H ₂ Ru ₄ (CO) ₁₃	1.87	2.39		60.15	154	bsb	13	[CpW(CO) ₃] ₂ - Mo(C- <i>tolyl</i>) ₂	1.793	2.218	1.2	52.9	170.3	lsb-I	44
1.81		2.23		55.8	149			CpW(CO) ₂ - (CH ₂ C- <i>tolyl</i>)TiCp ₂	1.788	2.225	1.19	53.11	169.7			
1.93		2.34		57.8	144			Cp ₂ Mo ₂ (CO) ₄	1.776	2.072	1.213	45.78	173.4	lsb-I	45	
1.86		2.32		58.0	152				2.01	2.38	1.18	66.0	176.3	lsb-II	46	
1.77		4.00		123.0	168	t			2.01	2.44	1.10	67.6	174.5			
1.85		3.97		117.5	172				1.93	2.39	1.13	67.3	175.3			
1.77		3.48		97.4	170	t	13		2.04	2.49	1.24	68.7	177.4			
[Ph ₄ P ₂ N][FeCo- (CO) ₈]		1.86	3.41		93.0	178				1.89	2.35	1.155	64.8	169	lsb-II	47
C ₁₂ H ₁₆ Fe ₂ (CO) ₆		1.784	2.21		57.4	151.2	bsb	14	Cp ₂ V ₂ (CO) ₅	1.88	2.39	1.161	66.2	169		
(Me ₂ C ₂)H ₂ Fe ₂ - (CO) ₈		1.753	2.321		64.3	161.9	bsb	15	Cp ₂ Cr ₂ (CO) ₄	1.98	2.465	1.093	72.2	167.9	lsb-II	48
(CF ₃) ₂ C ₂ CO ₂ (CO) ₃ - (triars)	1.736	2.484		69.3	168	bsb	16		1.91	2.520	1.123	74.7	171.1			
Fe ₃ (CO) ₈ (Ph ₄ C ₄)	1.80	2.34		64.4	160	bsb	17		1.858	2.505	1.145	75.2	172.6			
	1.842	1.991		53.47	143.8	bsb	18	Mn ₂ (CO) ₅ (dpm) ₂	1.94	2.449	1.093	72.4	171.4			
Fe ₂ (CO) ₄ - (PhC ₂ C ₆ H ₄ C ₂ Ph)	1.771	1.988		53.6	148.2	bsb	19	[C ₅ Me ₅ Cr(CO) ₂] ₂	1.93	2.01	1.1	43.0	174.08	lsb-IV	49	
Cp ₂ Rh ₂ Fe ₂ (CO) ₈	1.741	2.388		65.9	166.4	bsb	20	CpW(CO) ₃ GaMe ₂	1.832	2.464	1.162	73.0	170.8	lsb-II	50	
	1.79	2.10		55.8	152	b	20		1.812	2.623	1.171	79.1	174.8			
	1.89	1.89		47.77	136	t		CpMo(CO) ₃ ZnBr(thf) ₂	1.77	2.382	1.14	62.0	172.0	lsb-III	51	
	1.78	3.65		115.4	175				1.87	2.578	1.21	67.1	176			
	1.79	2.96		84.5	174				1.85	4.054	1.18	123.5	176			
[Fe ₆ (CO) ₁₆ C] ²⁻	1.79	2.19		55.5		bsb	21		1.844	2.681	1.166	70.2	174.8			
	1.79	2.19		55.8				CpMo(CO) ₃ ZnCl(OEt) ₂	1.909	4.22	1.143	129.3	179.2	t		
	1.94	2.16		54.3					1.822	2.459	1.169	65.3	174.6	lsb-III	53	
	1.94	2.16		55.5					1.821	2.481	1.164	66.0	174.1			
Fe ₂ (CO) ₆ (Ph ₂ C ₂)	1.727	2.472		68.3	164.8	bsb	22	[CpMo(CO) ₃] ₂ Zn	1.821	3.942	1.151	122.0	178.1	t		
Fe ₂ (CO) ₆ (NTs)- (CMeC ₂ H ₄ OMe)	1.73	2.80		76.6	172.0	t	23		1.839	2.481	1.142	67.9	175.1	lsb-III	53	
Fe ₂ (CO) ₉	2.016	2.016		51.3	141.2	bsb	24	CpW(CO) ₃ Au(PPh ₃)	1.852	3.967	1.152	66.2	176.4	t		
	1.838			177.1		t			1.852	3.967	1.143	126.7	177.6			
Fe ₃ (CO) ₈ (C ₄ H ₈ S) ₂	1.76	2.55		67.3	167	bsb	25		1.85	2.609	1.15	71.0	172.0	lsb-III	54	
Fe ₃ (CO) ₉ (PMe ₂ Ph)	2.02	2.04		51.6	139.0	bsb	26	[CpW(CO) ₃] ₃ Ga	1.90	2.332	1.14	62.0	168.0			
	1.97	1.97		49.9	139.5				1.78	3.915	1.19	124.0	177.0	t		
Fe ₂ (CO) ₇ (C ₁₀ H ₈ N ₂)	1.8	2.37		61.8	160.5	bsb	27		1.85	2.63	1.16	68.7	173.0	lsb-III	55	
	1.89	2.09		52.1					1.78	2.56	1.22	67.2	176.0			
Fe ₃ (CO) ₁₂	1.78	3.43		102.9	157	t	28		1.80	2.55	1.15	65.8	174.0			
	1.74	3.14		87.8	163				1.79	2.54	1.22	65.5	174.0			
	1.69	3.16		89.9	166.7				1.78	2.51	1.22	65.2	177.0			
[FeRu ₃ (CO) ₁₂ NO] ⁻	1.837	2.873		73.8	170.4	bsb	29		1.79	2.54	1.21	66.1	176.0			
	1.835	2.749		69.7	167.5				1.77	3.913	1.20	119.2	174.0			
	1.833	2.797		71.8	169.2				1.81	4.019	1.18	121.0	176.0			
[Fe ₂ Cp ₂ (CO) ₃ - (CNHMe)] ⁺	1.94	1.95		49.78	140	b	30	(C ₃ H ₅)Fe(CO) ₃ Au(PPh ₃)	1.79	3.944	1.18	118.7	176.0			
									1.773	3.294	1.14	106.3	177.0	t	56	
									1.773	2.424	1.14	72.0	177.4			
									1.789	2.398	1.14	70.9	175.3			

^a *a*, *b*, and *e* are given in units of angstroms; θ and ψ , in degrees. The types are abbreviated as follows: t = terminal; b = bridging; bsb = bent semibridging; lsb = linear semibridging.

available for iron. As we found in the case of our earlier study,² when metals other than the reference metal (Fe) were considered, it proved important to adjust the observed bond lengths for any difference in covalent radii.^{5a}

We picked only well-determined structures in which positions for M₁, M₂, C, and O were reported. The method is not particularly sensitive to the accuracy of any individual structure since the conclusions are based on such a large amount of data. Figure

1 shows the labeling system we used. M₁ is the metal having the shorter and M₂ the longer adjusted distance to C₁. M₁-C is labeled *a*, M₂-C *b*, C-O *e*, the angle M₁-C-O θ , and the angle M₂-M₁-C ψ . Less important for our purposes are the M-M distance *c* and the M₂-O distance *d*; these do not appear in Table I.

As expected on the basis of Cotton's^{4a} work, terminal carbonyls (1), bent semibridging carbonyls (3), and symmetrically bridging carbonyls (2) constitute a smooth continuum in which the value of the M₂-M₁-C angle, ψ , falls from ca. 125 to ca. 40° as the terminal carbonyl swings round on its way through the semibridging form to the ultimate symmetrically bridged state. This is represented most clearly in Figure 2 (the data points are shown as open circles), which shows how the M₁-C-O angle, θ , responds

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(55) Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* 1975, 1945.

(56) Simon, F. E.; Lauher, J. W. *Inorg. Chem.* 1980, 19, 2339.

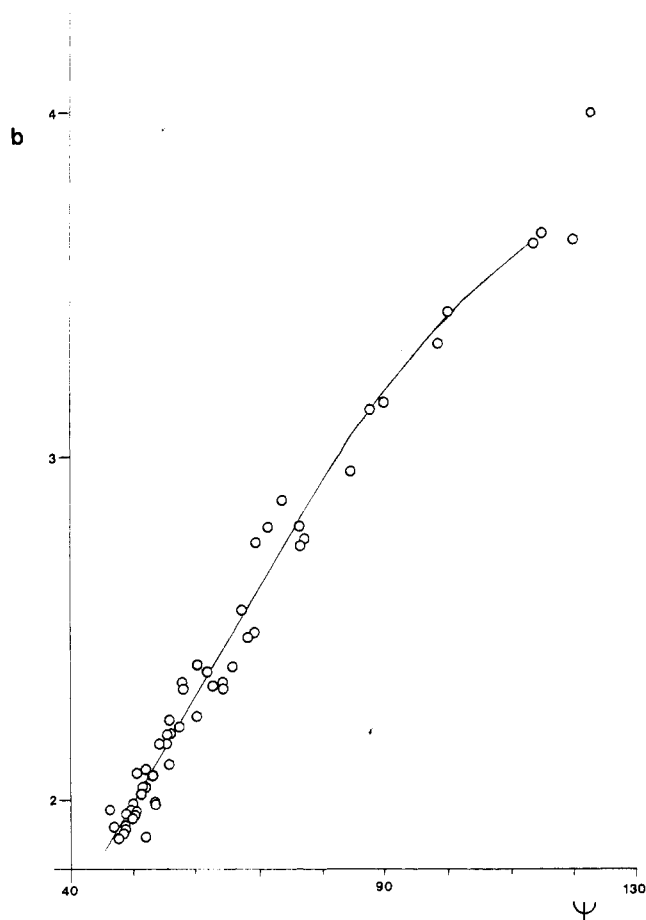


Figure 3. b vs. ψ for the bent semibridging, bridging, and terminal carbonyls.

to changes in the M_2-M_1-C angle, ψ . On the left side of the plot lie the symmetrically bridged species, for which ψ is ca. 49° and θ is ca. 138° . At first, when ψ is increased, θ also increases. This corresponds to the semibridging region. Surprisingly, the change of θ with ψ is essentially linear and appears to be governed by the empirical relationship of eq 1. At a θ value of 180° , this equation

$$\theta = 1.51\psi + 64.5 \quad (1)$$

extrapolates to $\psi = 76.5^\circ$, which implies that this ca. 75° angle marks the frontier between semibridging and terminal carbonyls. ψ is a better indicator of bridging than θ because an angle involving two heavy atoms and one light atom (ψ is M_2-M_1-C) is usually better determined crystallographically than is an angle involving two light atoms and one heavy one (θ is M_1-C-O). θ only falls below 170° at a ψ value of 70° , and so only at lower ψ does θ for the semibridging carbonyl fall significantly below the values that are seen in terminal structures. The random character of the θ values at $\psi > 75^\circ$ is confirmed by the fact that the direction in which the CO bends seems, on detailed study, to be dictated by steric effects rather than by the location of M_2 . In contrast, at $\psi < 75^\circ$ the CO tends to bend away from M_2 . This means that for the range of ψ values from 70 to 75° , bent semibridging, linear semibridging (see below), and terminal CO groups cannot be unambiguously distinguished.

The M_2-C distance b also varies in a regular way with ψ (Figure 3). This is unsurprising because it is largely a reflection of the geometry of the situation. The importance of this plot is that it enables us to tell what b value corresponds to the $\psi = 75^\circ$ bridging threshold. This turns out to be 2.69 \AA , which is 0.75 \AA longer than the sum of the covalent radii of C and Fe but considerably shorter than the sum of the corresponding van der Waals radii (ca. 3.5 \AA). In the C-H...M system, we found that the C-H bond began to show perturbations when it approached within 0.7 \AA of the covalent radii sum, a value close to that found here. On the other hand, in the symmetrical bridge the corre-

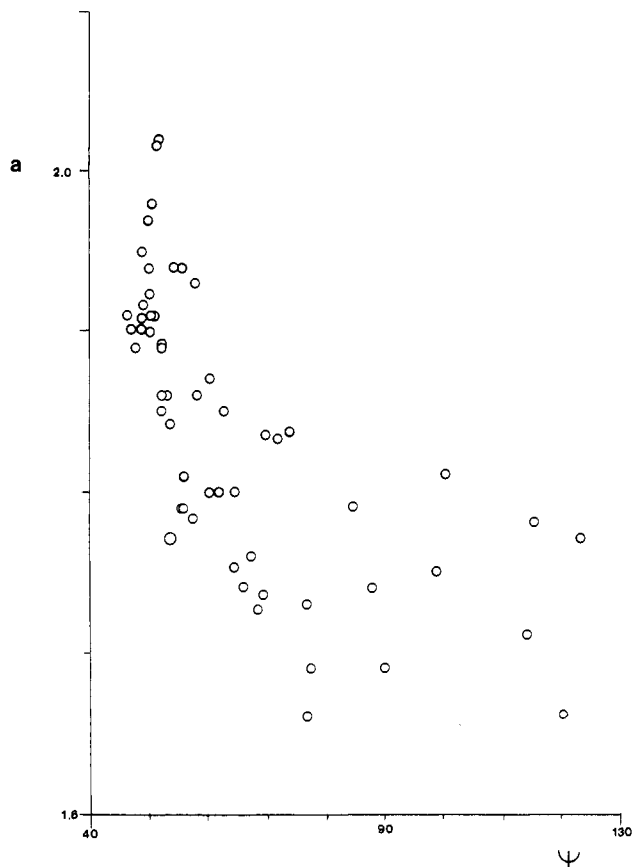


Figure 4. a vs. ψ for the bent semibridging, bridging, and terminal carbonyls.

Table II^a

ψ	θ	a	e	b	r_{sb}
50	138.8	1.964	1.24	1.98	0.04
55	147	1.898	1.22	2.145	0.205
60	155.2	1.832	1.20	2.31	0.37
65	163.4	1.766	1.179	2.475	0.535
70	171.6	1.733	1.158	2.63	0.69
75	179.8	1.733	1.13	2.69	0.75
80	180	1.730	1.13	2.83	
90	180	1.730	1.13	3.09	
100	180	1.730	1.13	3.33	
110	180	1.73	1.13	3.55	
120	180	1.73	1.13	3.74	
130	180	1.73	1.13	3.9	

^a Units are as in Table I.

sponding distance is 1.96 \AA , almost exactly the sum of the covalent radii. Figure 4 shows the way in which the M_1-C distance, a , varies with ψ . In the symmetrically bridging case (to the left on the plot) we have what is usually thought to be a single M-C bond. As ψ increases, the bond length falls, consistent with an increase in the M_1-C bond order. Above 70° , the distance is that of a terminal M-CO bond. Plots of b and a against θ were much less useful and showed poorer correlations.

Neither the CO bond length, e , nor the M-M bond length, c , varies systematically with ψ . The scatter in both cases is as great as any trends in the data. The C-O bond distance is probably not sufficiently well determined in these structures to act as a sensitive indicator of C-O bond order. In the case of the M-M bond, there is little reason to expect a change in the order. These data are entirely consistent with the currently accepted bonding picture,⁷ in which the CO carbon rehybridizes from sp to sp^2 in order to direct an acceptor orbital toward M_2 ; M_2 in turn donates electron density to this carbon.

From the data of Figures 2-4 it is possible by the Bürgi-Dunitz method¹ to define a reaction trajectory for terminal-bridge-terminal CO exchange between two iron atoms.^{4a} We have repre-

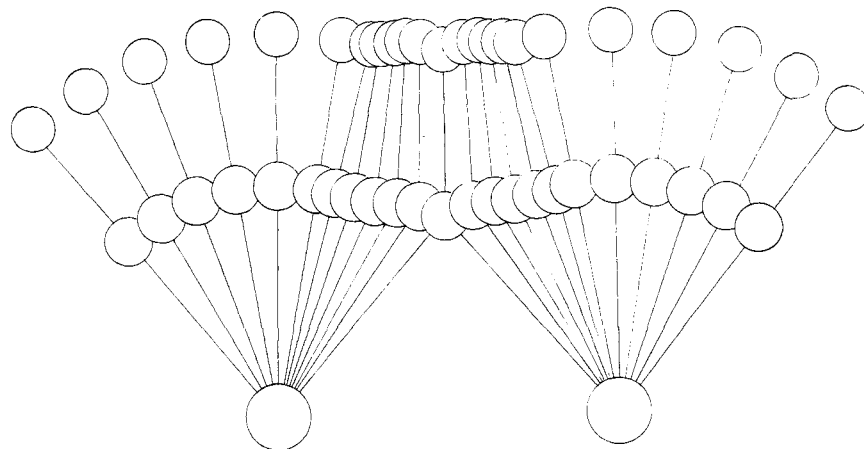


Figure 5. Reaction trajectory for the terminal-bridge-terminal carbonyl exchange between two iron atoms as deduced from the data of Figures 2-4.

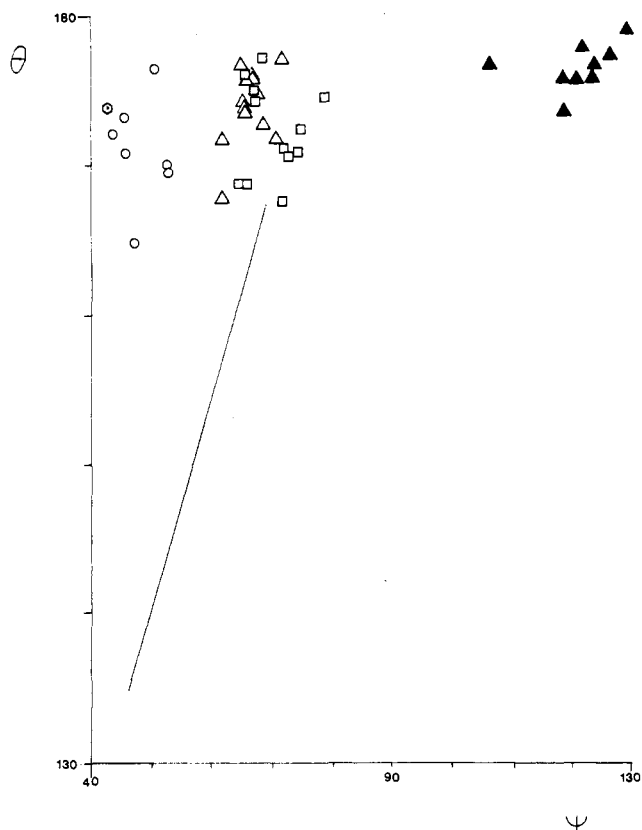


Figure 6. θ vs. ψ for linear semibridging carbonyls: type I, open circles; type II, open squares; type III, open triangles; type IV, open hexagon. For the type III cases, terminal carbonyls on M_1 are plotted as solid triangles. Equation 1 is also plotted for comparison.

sented the trends in the data as curves in Figures 2-4 and in numerical form in Table II. Figure 5 shows the resulting trajectory. Symmetrically bridging (2) and terminal CO's (1) are statistically much more common than semibridging cases (3), but among the semibridging groups, no particular value of ψ seems to be favored. This confirms the usual expectation that CO exchange is a facile process with a broad low-energy maximum separating the more stable structures 1 and 2. The C and O trajectories are both very smooth except for a slight but definite dip at the symmetrical structure.

The choice between terminal and bridging positions is not complicated by electron-count considerations in that the electron count of the cluster is unchanged on moving to the bridging form. On the other hand, the bridging form, which is known to be more basic at oxygen, is probably also more electron-withdrawing with respect to the cluster than is the terminal form. Bridging has therefore been proposed^{4a,b} as a way for the cluster to delocalize excess negative charge onto the ligands, and semibridging as a

way for the cluster to fine tune this delocalization.

The Linear Semibridging Carbonyl. Less well understood is the problem of the linear semibridging carbonyl (4). This appears to be distinct from any of the forms 1-3 because the M_1-C-O group remains linear on bridging. We therefore specifically looked for such structures to see if any further insight could be gathered from a systematic study of the structural details.

As demonstrated by Curtis^{4c} on a smaller series of compounds, θ varies with the asymmetry parameter in a different way for linear and bent semibridging CO groups. Our own results (Figure 6) confirm that the linear semibridging carbonyls have the θ values (160-180°) appropriate to terminal carbonyls but ψ values (40-75°) appropriate to semibridging ones.

The original suggestion^{4c} that these bridging CO's are 2-electron donors to M_2 has been reassessed in the light of recent theoretical studies, notably by Hoffmann et al.,⁶ by Hall et al.⁷ on $Cp_2M_2-(CO)_4$ structures, and by Benard, Dedieu, and Nakamura⁸ on $Mn_2(dppm)(CO)_5$. In the case of the $Cp_2M(CO)_4$ dimers, the metal fragments would, as far as the 18-electron rule goes, be triply metal-metal bonded if the CO's were not bridged. Hoffmann⁶ in particular has stressed how, in the semibridged form, the M-M bonding is now expressed through the bridging CO's. This happens by donation from d orbitals on M_2 to the CO π^* orbital, to form what can be regarded as a 3-center, 2-electron bond between M_1 , C, and M_2 . An analogy can be drawn with the C-H...M bridge,³ another situation where C-M bonding is expressed through the ligands via a 3-center, 2-electron bond. An alternative way of looking at this model of the linear CO semibridge, as stressed by Hall⁷ and by Dedieu,⁸ is to regard the CO π^* orbital as the acceptor and the M_1-M_2 π -bond as the donor in an acid-base interaction (5a). This seems to be essentially equivalent to the Hoffmann 3-center, 2-electron picture (5b). In this view, the



CO remains linear so that it can overlap with a π -component of the M-M multiple bond, not simply with M_2 as in the bent case, where sp to sp^2 rehybridization improves the overlap. The $M_2 \cdots O$ interaction is believed to be weak in these linear semibridging systems, even though the corresponding distance is short. Unlike bond distances for first-row main-group atoms, internuclear separations involving a heavy metal are not necessarily good indicators of the corresponding bond order. As will be seen in what follows, our studies suggest this model is not valid for all examples of linear semibridging CO.

Examination of the data for the linear semibridging systems (Figures 6-8) shows that the data points tend to congregate around certain values of ψ , θ , a , and e . Closer examination reveals the presence of three distinct clusters of data, which we interpret as implying the existence of three distinct structural types. Each of these types also differs in that each contains a distinctive

Table III

description	ψ , deg	θ , deg	a , Å	e , Å	M_2^a	n^a	M-M ^b	direction of bending of M ₁ -C-O
terminal	75	165-180	1.65-1.83	1.07-1.23	any	any		random
symmetrical bridging	49	136	1.85-2.00	1.17-1.23	transition metal	any		away from M ₂
bent semibridging	50-75	136-180	1.65-1.9	1.12-1.25	transition metal	any		away from M ₂
type I linear semibridging	40-55	165-180	1.70-1.80	1.2-1.25	early transition metal	1	long	toward M ₂
type II linear semibridging	60-72	165-180	1.80-2.05	1.08-1.25	transition metal	2-4	short	away from M ₂
type III linear semibridging	60-75	165-180	1.75-1.95	1.13-1.23	main group	any		away from M ₂ ^c
Mn ₂ (CO) ₅ (dppm) ₂	43	165-180 (?)	1.93	1.1 (λ)	late transition metal	1		away from M ₂

^a n = number of semibridging CO groups per M-M bond. ^b The M-M distance is normal for a single bond unless stated. ^c But see text.

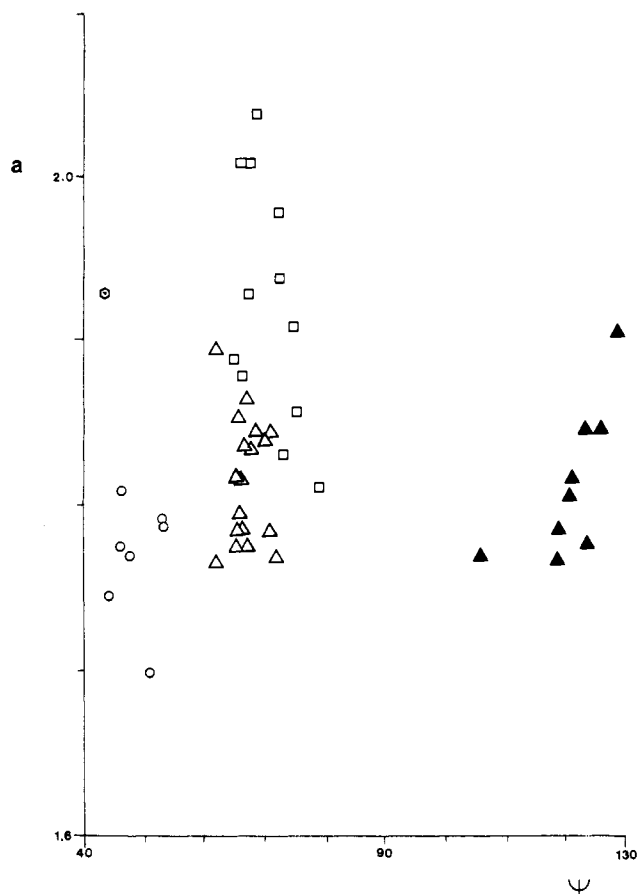


Figure 7. a vs. ψ for the linear semibridging cases, plotted as in Figure 6.

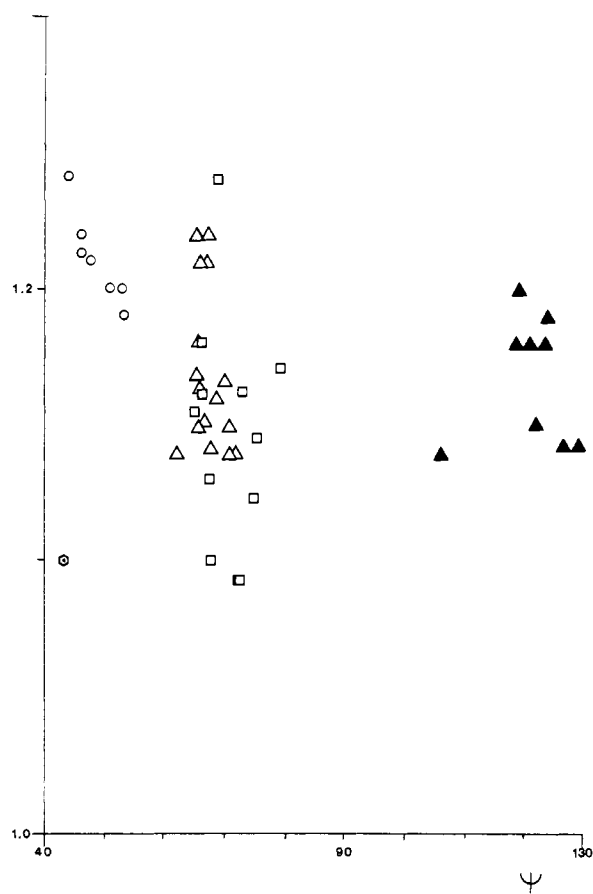


Figure 8. e vs. ψ for the linear semibridging cases, plotted as in Figure 6.

combination of metals M_1 and M_2 from different parts of the periodic table. A single complex falls outside these data clusters. We tentatively assign it to a fourth type but accept that this single example could easily be an artifact. These types are listed in Table III, where they are also compared with the classical types of carbonyl. In Figures 6-8, the different types are represented as follows: I, open circles; II, open squares; III, open triangles; IV, open hexagon.

(i) **Type I.** These systems are characterized by having an early transition metal for M_2 . Compared with the other types, the structures show a low ψ (Figure 6), a short a (M_1 -C; see Figure 7), and a long e (C-O; see Figure 8). This suggests that the 3-center, 2-electron model (5) is not valid for these systems. If it were, one would expect a long a and a long e as is found for type II, where we and others^{6,7} believe this model does hold. The lower ψ may result from the fact that type I systems have only one CO per M-M bond, while type II systems have two or more, diluting the interaction with each CO.

The a values are shorter than those for terminal CO's in the cases where these are also present. They are also shorter than

$M=C$ distances in alkylidene complexes. All other types of semibridging CO tend to bend away from M_2 (when seen in projection on the M_1CM_2 plane); type I carbonyls bend toward M_2 in such a way as to bring the carbonyl oxygen closer to M_2 . The fact that M_2 is always an oxophilic early transition metal suggests that this oxygen may indeed be binding to M_2 . The original bonding model of Curtis^{4c} (6b) may therefore be essentially



correct for type I. Contributions from each of the two forms 6a and 6b shown would account for all the structural peculiarities of type I: a short a , a long e , and the bending of the CO toward M_2 . Another indication of the importance of the contribution of 6a to the structure is the long M_1 - M_2 distances c found in type I structures; these are 0.3-0.47 Å longer than the sum of the covalent radii for the metals involved.

Theoretical work on type I species would be valuable, because none have been reported to date.

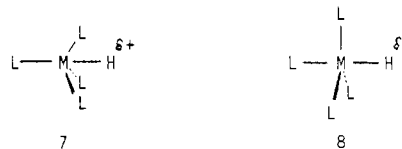
(ii) **Type II.** This type contains most of the classical examples of the linear semibridging carbonyl. Theoretical work has appeared on these systems,^{6,7} and the structural analysis is consistent with the 2-electron, 3-center model **5**. In particular both a and, to some extent, e tend to be long. ψ is quite large (60–72°). As mentioned above, this may be a result of having 2–4 CO's per M–M bond. More importantly, M–M bonds in this type would be multiple if the compounds had no CO bridges. This may mean that the CO's do not need to adopt a conformation of low ψ because the M–M bonding electrons of a multiple bond have significant electron density considerably above and below the midpoint of the M–M vector. These electrons can therefore interact with the CO π^* orbital even when ψ is as large as 70°. The semibridging CO therefore does not need to lean over as far to interact with M_2 via the M_1 – M_2 multiple bond.

In spite of the success of this model, we have also explored alternatives. The argument could be made that these type II carbonyls are merely bent semibridging groups having a large ψ and therefore a θ very near 180°. A careful comparison of Figure 6 with Figure 2 reveals that the data points for these type II species do indeed fall among, or very close to, those for the bent semibridging systems. Moreover, detailed examination of the type II structures shows that the CO's bend away from M_2 in each case, just as an incipient bent semibridging CO would be expected to do. The flaw in this argument, and the reality of the distinction between bent and type II linear semibridging carbonyls, emerges from a comparison of Figure 7 with Figure 4. This shows that the a values for type II structures are longer than would be expected for a bent semibridging structure having the same value of ψ . This is consistent with what would be expected on the basis of the accepted bonding model **5**. In the case of $[(C_5Me_5)Cr(CO)_2]_2$,⁵⁰ the observed a values just fall into the top of the range found for the bent structures; the semibridging interaction in this case is probably the smallest of all the type II structures.

(iii) **Type III.** The distinguishing characteristic of the type III semibridging systems is that they contain, in the M_2 position, a metal not known to form stable carbonyls, i.e., either Au or a main-group element such as Ga or Zn. These would not be expected to donate electrons efficiently to the CO π^* system. We therefore have to consider alternatives to the standard model. Are these systems best seen as linear semibridges, or can they more usefully be considered in another way? Could type III really represent an incipient bent semibridge? Examination of the type III structures shows that the CO's do not systematically bend away from M_2 . A particularly interesting case is that of $[Cp(CO)_3MoZnCl(OEt_2)]_2$,⁵³ in which the "semibridging" CO's seem to be bending away from the bulky Et_2O ligand bound to zinc, rather than from the zinc itself. As can be seen in Figure 6, ψ for type III systems is 10–15° larger than would be expected for a bent semibridge having the same ψ value. If they are not bent semibridges, could they be considered as type II linear semibridges? The arguments against this alternative seem to be as strong. type III systems do not have the multiple M_1 – M_2 bonds of type II systems. The M_1 –C distance a gives the initial impression of being long, but a comparison with the a values for unambiguously terminal CO's in the same structure (solid triangles in Figure 7) shows that they are entirely comparable. Any lengthening is therefore not due to bridging. Values of θ and e for semibridging and terminal CO's in the same molecule are also comparable (Figures 6 and 8).

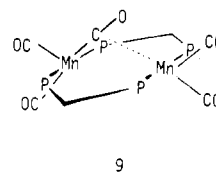
Terminal and semibridging CO's in these systems are structurally indistinguishable with respect to θ , a , and e . It therefore seems to be most useful to regard type III semibridges as terminal CO's that happen to have a low ψ . In order to be satisfied on this point, however, we would like to have some positive reason for the small ψ values that are observed.

Such a reason is provided by the work of Lauher,⁹ who has demonstrated a structural relationship between the H and Au-(PPh₃) groups. Briefly summarizing his argument, a L_nM –H or L_nM –Au(PPh₃) complex is considered as being formed from the L_nM^+ and H^- or $Au(PPh_3)^+$ units. Considering the M–H systems first, if the complex has $M^{\delta+}$ – $H^{\delta-}$ character (7), the L_nM fragment



will not need to rehybridize much on forming the M–H bond, and the structure of the complex as a whole will be very similar to that of the ML_n^- system, typically an n -vertex polyhedron. This implies that H–M–L angles will be small. On the other hand, if $M^{\delta+}$ – $H^{\delta-}$ is more appropriate (8), rehybridization to an $n + 1$ vertex polyhedron takes place, and H–M–L angles will be greater. Lauher found the $AuPPh_3$ group behaves like a δ^+ type of H. This implies that small L–M–Au ($=\psi$) angles will be found in type III complexes containing Au. We just need to extend this idea to the cases of $-ZnCl(OEt_2)$ and $-GaMe_3$ to understand the small ψ values in these cases, too. The result is that the ψ values can be small even if the bridging interactions are negligible. Other than this study by Lauher,⁹ no theoretical work appears to have been done on type III complexes.

(iv) **Type IV.** There is one further structure (9) that deserves mention because it does not fit into any of types I–III. Although



it constitutes only a single example at present, further ones may be discovered in the future. We tentatively assign it to a new class, type IV (plotted as an open hexagon in Figures 6–8). More than a single structure will be required before the reality of a new type can be confirmed. Like type I, it has a low ψ (43°) (Figure 6), but unlike this type it has a long M_2 –C bond, a (Figure 7), and a short C–O bond, e (Figure 8). This can be partially rationalized as follows. Since there is only one CO per M–M bond, the interaction is strong and ψ is correspondingly small. M_2 , as a late transition metal (Mn), is well able to donate to the CO π^* orbital in a 3-center, 2-electron interaction and M_1 –C is therefore longer than for type I. We do not understand the shortness of the C–O distance 1.10 (4) Å, which is unexpected. In view of the rather large esd and the fact that this is a single example, we tend to think this may be an artifact.¹⁰ Alternatively, an as yet unexplained feature of the bonding may be involved. Further crystallographically characterized examples of this type may be needed before this question is settled. Synthetic work directed toward the discovery of further type IV systems would be of particular value. Large numbers of systems forming A-frame structures are known for many different metals, and it is among these that such a search might be started.

Conclusion

In spite of many decades of work, metal carbonyl chemistry still presents a surprising number of problems that have yet to be solved to the satisfaction of a majority of workers in the field. We hope that this paper will be of some value in providing a quantitative way of systematizing data so that new structures can more readily be compared with the old. We have also been able to suggest types of structure that would make useful synthetic targets and others that merit theoretical study.

Our main conclusions on the characteristics of the different structural types of the linear semibridging carbonyl system are embodied in Table III. We expect that future structural studies of this sort may help to cast light on other important functional groups of inorganic chemistry.

Experimental Section

The data for a – e , θ , and ψ were obtained from the original literature cited in Table I. When the derived parameters we required were not given by the original authors, we occasionally had to calculate them from the crystal and atomic positional data. A correction for covalent-radius differences between the particular element, E, involved and the reference

element, iron, was obtained by adding the covalent radius of E minus the covalent radius of Fe to the values of the appropriate (Figure 1) bond lengths to obtain a , b , c , or d . The results were tabulated (only the more significant distances and angles a , b , e , θ , and ψ appear in Table I) and entered on a VAX computer, programmed to plot a , b , c , d , e , and θ or ψ against ψ or θ . The most significant of these plots are reproduced here as Figures 2-4 and 6-8. For the structural types 1-3, the trends of the data were extracted (Table II) and the result was plotted as Figure 5. This treatment resembles that in our work on the C-H...M group and derives from the Bürgi-Dunitz method. Deliberate care was taken to

avoid any bias in choosing the structures for study. Data points were not selectively eliminated to "improve" the appearance of Figures 2-8. Assignment to the different types was based on the criteria described in the text. Some assignments of bent semibridging instead of linear semibridging II were essentially arbitrary in the overlap region described in the text. No data appear twice under two different types, however.

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Solution Structure and Dynamics of $\text{Co}_2(\text{CO})_6(\text{L}\text{L})$ and $\text{Co}_4(\text{CO})_8(\text{L}\text{L})_2$ Molecules

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The solution structure and dynamics of the molecules $\text{Co}_4(\text{CO})_8(\text{L}\text{L})_2$, where LL = bis(diphenylphosphino)methane, bis(dimethylphosphino)methane, and (dimethylphosphino)(diphenylphosphino)methane, have been determined by ^{13}C and ^{31}P NMR spectroscopy. The structure is derived from the C_{3v} structure of $\text{Co}_4(\text{CO})_{12}$ with four CO's replaced by the two di(tertiary phosphines). All eight carbonyls exchange at the same rate, indicating a concerted mechanism for the exchange process. The corresponding dimers, $\text{Co}_2(\text{CO})_6\text{L}\text{L}$, are also fluxional in solution, and for these molecules the slow-exchange limit could not be reached. The tetramers are synthesized directly, in high yield, by pyrolysis of the dimers.

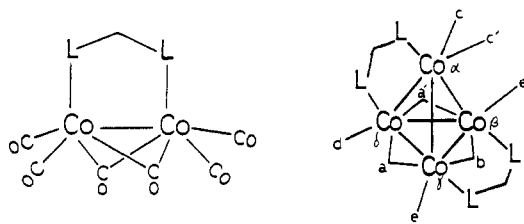
Introduction

The ability of bis(diphenylphosphino)methane, DPM, to form bridged binuclear complexes has led to increased interest in this and related ligands.¹ The reaction of $\text{Co}_2(\text{CO})_8$ with di(tertiary phosphines and arsines) is well-known to yield complexes of the formula $\text{Co}_2(\text{CO})_6(\text{L}\text{L})$.² A few of these have been characterized in the solid state and in solution.^{3,4} A crystal structure has been reported for the arsine derivative, $\text{Co}_2(\text{CO})_6(\text{C}_4\text{F}_4(\text{AsMe}_2)_2)$.³ Recently there has been some interest in derivatives of $\text{Co}_2(\text{CO})_6(\text{DPM})$ (1), namely $\text{Co}_2(\text{CO})_4(\text{DPM})(\mu\text{-alkyne})$ ⁵ and $\text{Co}_2(\text{CO})_4(\text{DPM})(\mu\text{-methylene})$,⁶ because of their solution dynamics. Also, cobalt complexes having bridging hydrido, phosphido, and iodo ligands have been synthesized from $\text{Co}_2(\text{CO})_6(\text{DPM})$.⁷

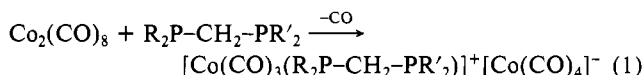
Here we discuss the synthesis, structure, and solution dynamics of the series of compounds $\text{Co}_2(\text{CO})_6(\text{DPM})$ (1), $\text{Co}_2(\text{CO})_6(\text{DMPM})$ (2), $\text{Co}_2(\text{CO})_6(\text{DMM})$ (3), $\text{Co}_4(\text{CO})_8(\text{DPM})_2$ (4), $\text{Co}_4(\text{CO})_8(\text{DMPM})_2$ (5), and $\text{Co}_4(\text{CO})_8(\text{DMM})_2$ (6); DMM = bis(dimethylphosphino)methane, DMPM = (dimethylphosphino)(diphenylphosphino)methane.

Results and Discussion

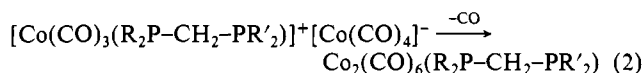
Synthesis. It is well-known that the reaction of certain phosphine and phosphite ligands with dicobalt octacarbonyl leads to rapid disproportionation.^{8a} Very bulky phosphine and arsine ligands react more slowly by a dissociative pathway to yield the neutral dimers $\text{Co}_2(\text{CO})_6\text{L}\text{L}$ directly.^{8b} In the case of the di(tertiary phosphines) we find that the addition of LL to $\text{Co}_2(\text{CO})_8$ gives the salt $[\text{Co}(\text{CO})_3(\text{L}\text{L})]^+[\text{Co}(\text{CO})_4]^-$ according to eq 1. This



- | | | | |
|---|------------|---|------------|
| 1 | L-L = DPM | 4 | L-L = DPM |
| 2 | L-L = DMPM | 5 | L-L = DMPM |
| 3 | L-L = DMM | 6 | L-L = DMM |



reaction is rapid and is over in a matter of minutes, as indicated by infrared spectroscopy. The reaction to form the neutral dimers, eq 2, is much slower, again as monitored by infrared spectroscopy



of the reaction mixture. With the bulky di(tertiary phosphine) DPM, the neutral dimer is seen quite rapidly so that it is not possible to rule out some substitution by a dissociative pathway^{8b} for DPM. For the ligands DPM, DMPM, and DMM, the approximate half-lives for reaction with $\text{Co}_2(\text{CO})_8$ to yield $\text{Co}_2(\text{CO})_6(\text{L}\text{L})$ are 5 h, 1 day, and 4 days, respectively. As a general rule, bulky substituents on the di(tertiary phosphine) favor small-ring formation,⁹⁻¹¹ and it is therefore expected that the intermediate chelate complex should be more stable when DPM is used than DMM. However, in the synthesis of $\text{Co}_2(\text{CO})_6(\text{L}\text{L})$ the ligands DMPM and especially DMM stabilize the intermediate salt. This is reasonable due to the increased basicity of these ligands. With bis(dimethylphosphino)methane it is possible to isolate $[\text{Co}(\text{CO})_3(\text{DMM})]^+[\text{Co}(\text{CO})_4]^-$ as a purple crystalline solid. Although reasonably pure when first isolated, the salt slowly

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