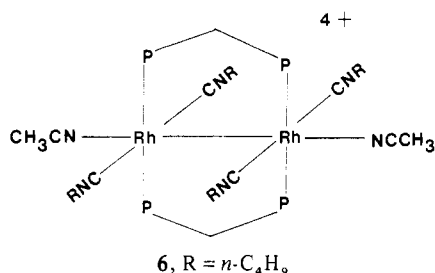
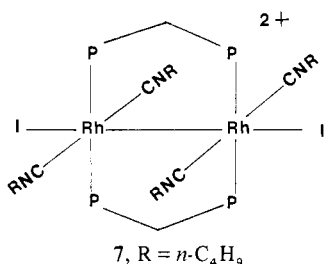


Controlled-potential coulometry at +1.30 V corresponds to the total transfer of two electrons ($n = 1.94$) per dimer cation for the two oxidation processes. If the initial sweep on an oxidized solution of **2** is in the positive direction, the two oxidation peaks no longer appear. When the sweep is reversed at +1.60 V, two reduction peaks occur, one at -0.20 V and one at -0.32 V. On the second positive sweep, two oxidation peaks occur near the potentials of the oxidation peaks of the parent rhodium(I) complex (Figure 3b). An unexplained third oxidation peak also appears. The rhodium(II) dimer formed by oxidizing **1** at +1.00 V in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$ is tentatively assigned structure **6**. The formation of a Rh-Rh bond is



consistent with other Rh(II)-Rh(II) species^{2,3} and makes each rhodium an 18-electron system. When Bu_4NI is added to the oxidized solution containing **6**, the solution turns from yellow to red and the UV-visible spectrum of the resulting solution is identical with that reported² for $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4\text{-(DPM)}_2\text{I}_2][\text{PF}_6]_2$, which has been formulated as **7**. This observation supports the conclusion that **6** is the product of the oxidation of **1**.



Acknowledgment. We thank the Research Corp. and Dow Corp. for support of this work. We acknowledge the Instrumentation Division of the NSF for funds that facilitated the purchase of the FT IR spectrometer. P.D.E. thanks the Chemistry Division of Oak Ridge National Laboratory for financial assistance in the form of a graduate stipend. The authors also express their gratitude to Professor J. Q. Chambers (University of Tennessee) for many helpful comments.

Registry No. **1**, 61160-69-8; **2**, 86527-12-0; **3**, 61160-73-4; **4**, 86527-13-1; **5**, 61160-76-7; **6** (X = BF_4^-), 86527-15-3; **7** (X = BF_4^-), 61160-83-6; Rh, 7440-16-6; Bu_4NBF_4 , 429-42-5; Bu_4NI , 311-28-4; Bu_4NPF_6 , 3109-63-5.

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

Relationship between the Metal-Metal Distance and the Nature of the Ligands in Dimers Doubly Bridged by Carbonyl, Nitrosyl, or Carbene Groups

Frank Bottomley

Received June 1, 1982

Over the last 15 years a large number of dimeric complexes

of general formula $[(L_nM)(L_mM')(\mu\text{-AB})_2]$ have been prepared, where L is a unidentate or one tooth of a polydentate ligand, n and m are 3 or 4, M and M' are transition metals (M may be the same as M'), and AB is a bridging ligand in which the atom A actually bridges the metal atoms. The bridging ligand may be a wide variety of π -acceptor or π -donor ligands, but the present analysis is confined to the cases where AB is a π -acceptor ligand, usually CO or NO though methylene bridges are becoming more common. Because we are interested in electronic effects and do not wish to be burdened with steric uncertainties, only dimers in which the two bridging AB ligands are independent will be considered; this precludes acetylene-bridged dimers among others. In Table I are listed the parameters of the 38 dimers of the type under consideration that have been structurally characterized.

Various aspects of these dimers have been discussed previously. In particular, the M-M bond distances and their relation (or lack of relation) to the number of electrons around M has received attention,¹⁻³ as have the puckering and asymmetry in the $\text{M}(\mu\text{-AB})_2\text{M}$ ring.³ The previous investigations have concentrated on a few of these dimers having closely related structures. We wish here to discuss a more general approach to the M-M and M-A distances in all of the known dimers.

The dimers in Table I fall into three groups. Considering only dimers containing first-row transition metals, inspection of the first four columns of Table I shows that those in group A have M-M distances of $2.36 \pm 0.03 \text{ \AA}$, M-A distances of $1.82 \pm 0.05 \text{ \AA}$, and MAM angles of $80.8 \pm 2.0^\circ$. Dimers in group B have M-M distances of $2.54 \pm 0.05 \text{ \AA}$, M-A distances of $1.93 \pm 0.03 \text{ \AA}$, and MAM angles of $82.6 \pm 2.0^\circ$. Dimers in the third small group, group C, have M-M distances of $2.46 \pm 0.06 \text{ \AA}$ while the M-A distances are markedly unequal on each side of the bridge (unlike dimers of groups A and B) and the MAM angles vary from 68.7 to 86° . The average distances and angles quoted above are simple averages, without taking into account any structural differences between dimers nor correcting for the different covalent radii of M and A. These simple averages are given to show that the dimers fall naturally into three groups without making any assumptions whatever. In order to include the dimers containing Ru in the comparison and to correct for the differences in covalent radii, the M-A distances in group A have been normalized to the Co-C distance in (arbitrarily chosen) $[(\text{Cp}^*\text{Co})_2(\mu\text{-CO})_2]$ by using the covalent radii given in the footnotes to Table I. The normalized distances are given in column 5. For group B $[(\text{OC})_3\text{Co})_2(\mu\text{-CO})_2]$ was chosen as the standard. Simple normalization of the M-M distance using the metal covalent radii begs the question of whether there is an M-M bond (see below). Since there is no question that an M-A bond exists, the normalized M-M distances (column 6) have been obtained by using the normalized M-A distances and the observed MAM angle. The results of these normalizations are an average M-M distance in group A of 2.38 \AA (+0.12, -0.04 \AA), an average M-A distance of $1.83 \pm 0.05 \text{ \AA}$, and an average MAM angle of 81.3° (+2.5, -5.0 $^\circ$). In group B the average M-M distance is 2.55 \AA (+0.14, -0.05 \AA), the average M-A distance is $1.93 \pm 0.03 \text{ \AA}$, and the average MAM angle is 82.9° (+4.1, -2.0 $^\circ$).

From the averaged distances and angles the same conclusion is reached as was apparent from the raw data. The M-M and M-A distances in group A are much shorter than in group B. On the other hand, there is no significant difference in the angles, for which the ranges overlap.

- (1) Bernal, I.; Korp, J. D.; Reisner, G. M.; Herrmann, W. A. *J. Organomet. Chem.* **1977**, *139*, 321.
- (2) Cirjak, L. M.; Ginsburg, R. E.; Dahl, L. F. *Inorg. Chem.* **1982**, *21*, 940.
- (3) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654.

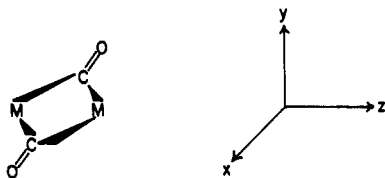


Figure 1. Coordinate system for $[(L_nM)(L_mM')(\mu-AB)_2]$ dimers.

Before advancing reasons for the differences between groups A and B, it is necessary to dispose of some obvious possible causes. First, steric effects are not a cause. Although most of the group B dimers are of the $[(L_4M)_2(\mu-AB)_2]$ type and most group A of the $[(L_3M)_2(\mu-AB)_2]$ type (of which the latter would be expected to have the least steric strain), $[(OC)_3Co)_2(\mu-CO)_2]$ appears in group B, not in group A, and $[(acac)_2Ru)_2(\mu-NO)_2]$ in group A, not in group B. Possibly the least sterically strained dimer of all $[(Cl_2Pd)_2(\mu-CO)_2]^{2-}$ has relatively long Pd-Pd and Pd-C distances. Steric repulsion would also be expected to have a marked effect on the MAM angle but rather less effect on the M-A distances. The opposite is observed. Steric strain does not explain the markedly different M-A distances within group C nor the large (>0.1 Å) differences between the M-A and M-M distances in $[(acac)_2Ru)_2(\mu-NO)_2]$ when compared to the $[(Cp(CO)Ru)_2(\mu-AB)_2]$ dimers in group B. Second, the differences between groups A and B are not due to the ring puckering (distortion of the $M(\mu-AB)_2M$ ring from planarity), which has been analyzed by Pinhas and Hoffmann.³ Column 7 of Table I gives the θ angle (as defined by Pinhas and Hoffmann) for the dimers. It is seen that examples of both strictly planar and very puckered dimers appear in both groups A and B, and there is no correlation between the puckering and the M-A or M-M bond distance. Third, although all the group B dimers have the 17-17-electron count (column 8), the gross differences in the M-M and M-A distances between groups A and B do not appear to be due to the number of electrons, since 17-17 counts appear in group A as well. There are small differences in the M-M and M-A distances within Group A. These have been discussed by Pinhas and Hoffmann³ and by Dahl and co-workers² and will be further discussed below. Fourth, it is clear that the exact nature of the AB bridge is not important to the gross differences between groups A and B; nitrosyl, carbonyl, thiocarbonyl, or carbene bridges are equivalent.

Bridged dimers of the types under discussion have been studied from a theoretical viewpoint previously.³⁻⁷ Pinhas and Hoffmann provided a model for the $[(CpM)_2(\mu-AB)_2]$ dimers predominant in group A.³ In this model the three frontier orbitals of a CpM fragment⁸ interact to form a CpM-MCp dimer now having five frontier orbitals^{9,10} that interact in turn with the bridging AB group orbitals. The important interactions, stated in terms of their metal orbital involvement and using the coordinate scheme shown in Figure 1 (C_{2v} symmetry) are shown in (1)-(5). Interactions 1 and 2 produce two

$$[(p_z - p_z) + 5\sigma(AB)_g] \quad (a_1) \quad (1)$$

$$[(d_{xz} - d_{xz}) + 5\sigma(AB)_u] \quad (a_1) \quad (2)$$

$$[(d_{xz} + d_{xz}) + \pi_z^*(AB)_g] \quad (a_2) \quad (3)$$

$$[(d_{yz} - d_{yz}) + \pi_y^*(AB)_u] \quad (a_1) \quad (4)$$

$$[(d_{yz} + d_{yz})] \quad (b_2) \quad (5)$$

low-energy filled $M(\mu-AB)_2M$ bonding orbitals of mainly AB character and two empty antibonding orbitals mainly metal in character. Of these antibonding orbitals the counterpart of (1) is at very high energy but the counterpart of (2)

$$[(d_{xz} - d_{xz}) - 5\sigma(AB)_u] \quad (b_1) \quad (6)$$

is the LUMO of the 17-17- and 17-16-electron dimers in group A. It may be described as an in-plane M-M π -bonding orbital. Interactions 3 and 4 provide $M(\mu-AB)_2M$ bridge bonding by π -back-donation of metal electrons into π^* orbitals on the bridge. The resultant molecular orbitals are in-plane (4) and out-of-plane (3) (with respect to the $M(\mu-AB)_2M$ plane) and are occupied in all the $[(CpM)_2(\mu-AB)_2]$ dimers in group A. Finally, the HOMO of the 17-17- or 17-16-electron dimers of the $[(CpM)_2(\mu-AB)_2]$ is the b_2 orbital, which by symmetry cannot interact with the frontier orbitals of the bridge and is best described as an out-of-plane M-M π -antibonding orbital.

For the present purposes the major result of this analysis (which has been given convincing support by Dahl and co-workers²) is that the only *direct* M-M interaction in a 17-17- or 17-16-electron dimer is an out-of-plane π -antibonding one. There is an interaction between the remnants of the t_{2g} set of metal orbitals, but this produces an equal number of bonding and antibonding orbitals whose energies exactly cancel.³ For a 16-16-electron dimer there is no direct M-M interaction at all. The halves of the $[(CpM)_2(\mu-AB)_2]$ dimer are held together by the 8 electrons in the four $M(\mu-AB)_2M$ bridge bonding orbitals (interactions 1-4 above). We stress (as has not been done before) that the major factor determining the M-M distances is not the number of electrons above 16-16, nor the metal per se, but rather the bridging unit. In essence, the M-M distance is determined primarily by the M-A distance and the MAM angle. Occupation of the b_2 orbital will result in a minor perturbation (lengthening) of the M-M distance but no major change. The MAM angle is effectively constant for all of the dimers in Table I because at 80° there is maximum overlap of the orbitals involved in interactions 1-4. The M-M distance in group A (which for the dimers containing first-row metals only ranges 0.03 Å on either side of the average) is therefore basically determined by the M-A distance (which ranges 0.05 Å on either side of the average).

Dahl and co-workers suggested that the lengthening in the Co(μ -CO) distance that accompanied the shortening of the Co-Co distance on removing an electron from the b_2 orbital of $[(Cp^*Co)_2(\mu-CO)_2]^-$ to give $[(Cp^*Co)_2(\mu-CO)_2]^0$ was due to the lowering of the energy of the metal atomic orbitals with the loss of negative charge.³ This resulted in a decrease in π -back-bonding to the CO bridging ligands (i.e., a decrease in interactions 3 and 4 above). This explanation suggests a general rule: the higher the energy of the metal atomic orbitals the shorter the M-A distance. With one exception this rule appears to work well and explains for instance why the Fe-N distance in $[(CpFe)_2(\mu-NO)_2]$ (1.768 Å) is less than in $[(CpCo)_2(\mu-NO)_2]$ (1.825 Å) despite the larger covalent radius of Fe compared to that of Co. The one exception is the decrease in the Co-N distance on going from $[(CpCo)_2(\mu-NO)_2]$ to $[(CpCo)_2(\mu-NO)_2]^+$ for which there is no explanation.

We now turn to the dimers of group B. The majority of these are of the $[(Cp(XY)M)_2(\mu-AB)_2]$ type, where XY is CO or NO. Such dimers have also been analyzed previously.⁴⁻⁷ The Cp(XY)M fragment provides only two frontier orbitals which in combining to give the $(Cp(XY)M)_2$ fragment give rise to three low-lying orbitals with which the frontier orbitals

- (4) Benard, M. *J. Am. Chem. Soc.* **1978**, *100*, 7740.
 (5) Benard, M. *Inorg. Chem.* **1979**, *18*, 2782.
 (6) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 3397. Mitschler, A.; Rees, B.; Lehmann, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 3390.
 (7) Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576.
 (8) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058, 365.
 (9) Burdett, J. K. *J. Chem. Soc., Dalton Trans.* **1977**, 423. Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103.
 (10) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

Table I

complex ^a	M-M, Å	M-A, Å	MAM deg	M-A dist (cor), ^b Å	M-M dist (cor), ^b Å	ring puckering, ^c deg	electron count	ref
Group A								
[(CpFe) ₂ (μ-NO) ₂]	2.326	1.768	82.3	1.78	2.34	180	16-16	<i>d</i>
[(Cp*Co) ₂ (μ-CO) ₂]	2.338 (2.327) ^e	1.851	78.4	1.85	2.34	176	16-16	<i>f</i>
[(CpCo) ₂ (μ-NO)(μ-CO)]	2.370	1.829	80.7	1.83	2.37	180	17-16	<i>g</i>
[(CpCo) ₂ (μ-CO) ₂] ^{-h}	2.372	1.82	81.2	}1.82	}2.37	180	17-16	<i>i</i>
[(CpCo) ₂ (μ-CO) ₂] ⁻	2.359	1.82	81.2					
[(CpCo) ₂ (μ-CO) ₂] ⁻	2.364	1.815	81.3			180		<i>f</i>
[(Cp*Co) ₂ (μ-CO) ₂] ⁻	2.372	1.827	81.0	1.84	2.39	168	17-16	<i>f</i>
[(CpCo) ₂ (μ-NO) ₂] ⁺	2.348	1.762	83.5	1.78	2.37	180	17-16	<i>j</i>
[(CpNi) ₂ (μ-CO) ₂] ^h	2.363	1.861	78.8	}1.875	}2.37	146	17-17	<i>k</i>
	2.351	1.869	78.1					
[(CH ₃ C ₅ H ₅)Ni] ₂ (μ-CO) ₂	2.390	1.564 ⁱ	79.7	1.85	2.37	180	17-17	<i>k</i>
[(CpCo) ₂ (μ-NO) ₂]	2.372	1.825	81.1	1.84	2.39	180	17-17	<i>g</i>
<i>trans</i> -[(<i>rac</i>) ₂ Ru] ₂ (μ-NO) ₂	2.614	1.918	85.9	1.84	2.51	180	17-17	<i>m</i>
Group B								
[(OC) ₃ Co] ₂ (μ-CO) ₂	2.524	1.920	83.0	1.92	2.54	127	17-17	<i>n</i>
<i>cis</i> -[(C ₆ H ₅) ₂ (CO)Co] ₂ (μ-CO) ₂	2.559	1.911	84.1	1.91	2.56	175	17-17	<i>o</i>
<i>trans</i> -[(C ₄ H ₄ (CH ₃) ₂)(CO)Co] ₂ (μ-CO) ₂	2.549	1.931	82.9	1.93	2.55	180	17-17	<i>p</i>
[(NBD)(CO)CoCo(CO) ₃ (μ-CO) ₂] ^q	2.531	1.929	81.9	1.93	2.53	135	17-17	<i>r</i>
[(Cp(CO)FeCo(NBD)CO)(μ-CO) ₂] ^q	2.530	1.909	82.9	1.91	2.53	161	17-17	<i>s</i>
<i>cis</i> -[(OC) ₃ CoFe(CO)Cp](μ-CO) ₂	2.545	2.036 (Co) 1.882 (Fe)	80.9	1.96 ^t	2.54	143	17-17	<i>u</i>
<i>trans</i> -[(CH ₃) ₂ C ₄ H ₄ (CO)FeCo(CO)(C ₄ H ₆)](μ-CO) ₂	2.546	1.949	82.6	1.95	2.57	180	17-17	<i>v</i>
<i>trans</i> -[(Cp(NO)Cr) ₂ (μ-NO) ₂]	2.615	1.960	86.7	1.96	2.69	180	17-17	<i>w</i>
<i>trans</i> -[(Cp(CO)Fe) ₂ (μ-CO) ₂]	2.534	1.914	82.9	1.92	2.54	180	17-17	<i>x</i>
<i>cis</i> -[(Cp(CO)Fe) ₂ (μ-CO) ₂]	2.531	1.916	82.6	1.93	2.55	164	17-17	<i>y</i>
<i>cis</i> -[(Cp(CO)Fe) ₂ (μ-CO)(μ-CS)]	2.505	1.900	82.5	1.91	2.52	166	17-17	<i>z</i>
<i>cis</i> -[(Cp(CO)Fe) ₂ (μ-CS) ₂]	2.482	1.906	81.2	1.92	2.50	163	17-17	<i>aa</i>
<i>trans</i> -[(Cp(CO)MnMn(NO)Cp)(μ-NO)(μ-CO)]	2.571	1.906	84.8	1.91	2.57	180	17-17	<i>bb</i>
<i>cis</i> -[(CpCp)((CO)Fe) ₂ (μ-CO) ₂] ^{cc}	2.510	1.922	81.8	1.93	2.53	160	17-17	<i>dd</i>
<i>cis</i> -[(Cp(CO)Fe) ₂ (μ-CO)(μ-CHCOO- <i>t</i> -Bu)]	2.505	1.920	81.9	1.93	2.53	162	17-17	<i>ee</i>
<i>cis</i> -[(Cp(CO)Fe) ₂ (μ-CO)(μ-CHCH ₃)]	2.525	1.946	80.9	1.96	2.54	166	17-17	<i>ff</i>
<i>cis</i> -[(Cp(CO)Fe) ₂ (μ-CO)(μ-CH ₂)]	2.511	1.92	81.5	1.93	2.52	NA	17-17	<i>gg</i>
[(Cp(CO)Fe) ₂ (μ-CO)(μ-C=CPh(CH ₂ Ph))]	2.510	1.934	80.9	1.94	2.52	180	17-17	<i>jj</i>
<i>trans</i> -[(Cp(CO)Ru) ₂ (μ-CO) ₂]	2.735	1.986	87.0	1.90	2.61	180	17-17	<i>hh</i>
<i>cis</i> -[(Cp(CO)Ru) ₂ (μ-CO)(μ-CCH ₃)] ⁺	2.714	1.993	85.6	1.90	2.58	165	17-17	<i>ii</i>
<i>cis</i> -[(Cp(CO)Ru) ₂ (μ-CO)(μ-C=CH ₂)]	2.695	2.034	82.9	1.94	2.57	159	17-17	<i>ii</i>
[(Cl ₂ Pd) ₂ (μ-CO) ₂] ²⁻	2.697	1.994	85.2	1.88	2.54	180	15-15	<i>kk</i>
Group C								
<i>trans</i> -[(Cp(NO)Mn ¹ Mn ² (NO) ₂ Cp)(μ-NO) ₂]	2.526	1.943 (Mn ¹) 1.775 (Mn ²)	85.5			NA	18-16	<i>ll</i>
<i>cis</i> -[(Cp(NO)Mn ¹ Mn ² (η ¹ -Cp)Cp)(μ-NO) ₂]	2.520	1.944 (Mn ¹) 1.752 (Mn ²)	85.8			NA	18-16	<i>mm</i>
[(CpNiCo(CO) ₂ (R ₃ P)(μ-CO) ₂] R = C ₂ H ₅	2.410	1.825 } Ni 1.900 } 1.956 } Co 1.890 }	80.6			134	17-17	<i>nn</i>
R = <i>p</i> -C ₆ H ₄ F	2.425	1.894 } Ni 1.823 } 1.904 } Co 2.026 }	81.4			134	17-17	<i>oo</i>
R = Ph ₂ C ₆ H ₁₁	2.418	1.862 } Ni 1.842 } 1.929 Co	81.5			134	17-17	<i>pp</i>
[(Cp(CO)V ¹ V ² (CO) ₂ Cp)(μ-CO) ₂]	2.462	1.936 (V ¹) 2.421 (V ²)	67.75			117	16-14	<i>qq</i>
[(CH ₃) ₃ P] ₃ Ru ₂ (μ-CH ₂) ₂ ²⁺	2.641	2.071	79.2			180	15-15	<i>rr</i>

^a Cp = η⁵-C₅H₅; Cp* = η⁵-C₅(CH₃)₅. ^b The following covalent radii were used in the correction (Å): C, 0.77; N, 0.75; V, 1.22; Cr, 1.18; Mn, 1.17; Fe, 1.17; Co, 1.16; Ni, 1.15; Ru, 1.25; Pd, 1.28. ^c Angle defined as in ref 3. ^d Calderon, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W.; Iske, D. A. *J. Organomet. Chem.* 1974, 64, C16. ^e Value in parentheses obtained by: Bailey, W. I.; Collins, D. M.; Cotton, F. A.; Baldwin, J. C.; Kaska, W. C. *Ibid.* 1979, 165, 373. ^f Reference 2. ^g Reference 1. ^h There are two independent molecules per unit cell in this dimer. ⁱ Shore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* 1977, 99, 1781. ^j Wochner, F.; Keller, E.; Brintzinger, H. H. *J. Organomet. Chem.* 1982, 236, 267. ^k Byers, L. R.; Dahl, L. F. *Inorg. Chem.* 1980, 19, 680. ^l Average value of two Ni-C distances. This dimer is quite asymmetric due to the (CH₃)₂C₄H₄ ligand. See ref *k*. ^m Bottomley, F.; Mukaida, M.; White, P. S. *Acta Crystallogr., Sect. B* 1982, B38, 2674. ⁿ Summer, C. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* 1964, 17, 732. ^o Stephens, F. S. *J. Chem. Soc., Dalton Trans.* 1972, 1752. ^p Stephens, F. S. *J. Chem. Soc. A* 1970, 2745. ^q NBD = norbornadiene. ^r Stephens, F. S. *J. Chem. Soc., Dalton Trans.* 1972, 1754. ^s Campbell, I. L. C.; Stephens, F. S. *Ibid.* 1975, 226. ^t Using average Co-C and Fe-C distances. ^u Campbell, I. L. C.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* 1975, 22. ^v Campbell, I. L. C.; Stephens, F. S. *Ibid.* 1974, 923. ^w Calderon, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. *J. Organomet. Chem.* 1974, 64, C10. ^x Bryan, R. F.; Green, P. T. *J. Chem. Soc. A* 1970, 3064. ^y Bryan, R. F.; Green, P. T.; Newlands, M. J.; Field, D. S. *Ibid.* 1970, 3068. ^z Beckman, D. E.; Jacobson, R. A. *J. Organomet. Chem.* 1979, 179, 187. ^{aa} Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. *Ibid.* 1976, 114, C49. ^{bb} Kirchner, R. M.; Marks, T. J.; Kristoff, J. S.; Ibers, I. A. J.

Footnotes to Table I (Continued)

Am. Chem. Soc. 1973, 95, 6602. ^{cc} CpCp = ($\eta^5\text{-C}_5\text{H}_5$)(CN(CH₃)₂)₂($\eta^5\text{-C}_5\text{H}_5$). ^{dd} Stevens, F. S. *J. Chem. Soc. A* 1970, 1722. ^{ee} Hermann, W. A.; Plank, J.; Bernal, I.; Creswick, M. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* 1980, 35B, 680. ^{ff} Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1980, 441. Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* 1981, 20, 3024. ^{gg} Korswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem.* 1981, 93, 1073. ^{hh} Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* 1967, 9, 339. ⁱⁱ Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *Ibid.* 1980, 198, C43. ^{jj} Hossain, M. B.; Hanlon, D. J.; Marten, D. F.; van der Helm, D. *Acta Crystallogr., Sect. B* 1982, B38, 1457. ^{kk} See ref 12. ^{ll} Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Martinez, N. J. *Chem. Soc., Chem. Commun.* 1971, 1476. ^{mm} Calderon, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W.; Stults, B. R. *Inorg. Chim. Acta* 1976, 17, L31. ⁿⁿ Campbell, I. L. C.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* 1975, 337. ^{oo} Campbell, I. L. C.; Stephens, F. S. *Ibid.*, 1975, 340. ^{pp} Stephens, F. S. *Ibid.* 1974, 1067. ^{qq} Cotton, F. A.; Kruczynski, L.; Frenz, B. A. *J. Organomet. Chem.* 1978, 160, 93. ^{rr} Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* 1979, 101, 4128.

of the AB bridge can interact.⁷ Two of the low-lying orbitals are the $p_x - p_z$ and $d_{xz} - d_{yz}$ combinations, and these interact with the $5\sigma(\text{AB})$ orbitals exactly as described above for the interactions 1 and 2 of the [(CpM)₂(μ -AB)₂] case. The third orbital is the in-plane $d_{xz} + d_{yz}$, giving rise to the same interaction as (3) above, and this is the HOMO of the final 17-17-electron [(Cp(XY)M)₂(μ -AB)₂] dimer. Missing from the [(Cp(XY)M)₂(μ -AB)₂] case as compared to [(CpM)₂(μ -AB)₂] are the out-of-plane interactions (4) and (5) because the d_{yz} orbitals are now required for bonding to XY. There is now no direct M-M interaction at all (again, the t_{2g} remnants interact to produce an equal number of bonding and antibonding orbitals that cancel). Note that since the M-M interaction ((5) above) is antibonding with respect to the M-M unit, its removal would be expected to shorten the M-M distance on proceeding from group A to group B. In fact, a large (0.15 Å for the raw data of first-row dimers, 0.17 Å for the normalized average) increase occurs. This is due to the proportionately even greater increase in the M-A distance (0.10 Å on average). The MAM angles remain essentially the same in group B as in group A. The increase in the M-A distance is due to two factors. First, in the [(Cp(XY)M)₂(μ -AB)₂] dimers only 6 electrons in 3 orbitals are available to hold the M(μ -AB)₂M bridge together, rather than the 8 electrons in 4 orbitals found for [(CpM)₂(μ -AB)₂]. Second, where the XY ligand is a π -acceptor (CO, NO), it has π^* orbitals of the correct symmetry to overlap with the $d_{xz} + d_{yz}$ combination, which gives rise to interaction 3 above. The XY ligand competes with the AB bridge for π -bonding from the metal. Since XY generally is the same as AB, the competition is very great. Hence, the M-A bond is much weakened and therefore lengthened compared to those in the [(CpM)₂(μ -AB)₂] dimers in group A. There are small differences in the M-A distances within group B dimers, but no trends can be discerned.

Very interesting support for the above ideas comes from the presence of [(OC)₃Co)₂(μ -CO)₂] in group B (because of its Co-C and Co-Co distances) whereas in terms of the isolobal analogy it belongs with the [(CpM)₂(μ -AB)₂] dimers of group A and has previously been analyzed as such.³ The crucial difference is that the three terminal CO ligands on each cobalt of [(OC)₃Co)₂(μ -CO)₂] can compete with the bridging CO ligand for π -bonding with CO, thus drastically weakening the bonding interactions (3) and (4) above. On the other hand [(acac)₂Ru)₂(μ -NO)₂], which is an [(L₄M)₂(μ -AB)₂] dimer of the type predominant in group B, has both an Ru-Ru and an Ru-N distance 0.1 Å shorter than the [(Cp(CO)Ru)₂(μ -AB)₂] dimers in group B and therefore appears in group A. The low π -acceptor capability of the acac ligand allows the in-plane bridge bonding to strengthen.

Further support comes from considering group C. One type of dimer in this group is represented by the formula [(CpNiCo(CO)₂(R₃P))(μ -CO)₂], in which the Cp on Ni cannot compete with the bridging CO for π -back-bonding but the terminal CO on Co can do so. The Ni-bridge bonding is not weakened whereas the Co-bridge bonding is, and this is reflected in the markedly unequal Ni-C- and Co-C-bridge

bond distances. Another type of dimer in this group is [(Cp(NO)Mn)(Cp(Z)Mn)(μ -NO)₂] (Z = NO₂, η^1 -Cp). Here, one Mn carries the π -acceptor ligand NO, the other carries the σ -donor NO₂⁻ or η^1 -Cp⁻ ligand, and as expected, the Mn-NO bridging distances are much longer for the Mn carrying the NO (1.944 or 1.943 Å) than for the Mn carrying Z (1.752 or 1.775 Å). Note that the bridge is symmetrical in *trans*-[(Cp(CO)(Mn))(Cp(NO)Mn)(μ -NO)(μ -CO)].

Also placed in group C is [(Cp(CO)V)(Cp(CO)₂V)(μ -CO)₂]. This is a dimer of the type [(L₄M)(L₃M)(μ -AB)₂], which has not been treated above. However, the principle is obvious. A dimer of type [(Cp(CO)₂M)₂] would have only one orbital available to interact with the frontier orbitals of the bridging AB fragment, and a further weakening of the bridge bonding (compared to [(Cp(CO)M)₂(μ -AB)₂]) can be expected. In addition, the presence of an additional π -acceptor terminal CO ligand to compete with the bridging CO for π -bonding will weaken the bridge bonding even more. No [(Cp(CO)₂M)₂(μ -AB)₂] dimers have been characterized as yet (they would be restricted to the group 3-6 metals or lanthanides). However, in [(Cp(CO)V)(V(CO)₂Cp)(μ -CO)₂] the principle is clearly operating; the bridge is markedly asymmetrical, with the V-C distance involving the V carrying two terminal CO ligands (2.421 Å) very much longer than that to the V carrying only one CO (1.936 Å). Note that the V-V distance, like all of those in group C, is intermediate between the group A and the group B M-M distances, as is expected from the presence of two types of bridge bond.

Also placed in group C is [(((CH₃)₃P)₃Ru)₂(μ -CH₂)₂]²⁺, which has a Ru-Ru distance intermediate between those of groups A and B but a very long Ru-C bridging distance. The latter would be expected since this is a 15-15-electron dimer and therefore has insufficient electrons to fill the bridge orbitals. However, the Ru-Ru distance in this molecule is not explained by our present argument.

The dimer [(Cl₂Pd)₂(μ -CO)₂]²⁻ has been placed in group B. Although there is no competition for π -back-bonding to the carbonyl bridge by the Cl ligands, previous work has shown that the bridge is held together by only three interactions ((1)-(3) above) not by four.¹¹⁻¹³ Because [(Cl₂Pd)₂(μ -CO)₂]²⁻ is the only dimer of its type, it is not yet possible to place it with certainty in any group, though both the Pd-Pd and Pd-C distances are closer to those of group B than those of group A.

We note finally that the ideas presented are only applicable

- (11) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 2074.
- (12) Goggin, P. L.; Goodfellow, R. J.; Herbert, I. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1981, 1077.
- (13) A further interesting example of a group C dimer appeared after submission of the manuscript. [(Cp(PMe₃)Co)(CpCo²)(μ -CS)₂] has Co-Co = 2.392 Å, Co-C = 1.947 and 1.960 Å, Co²-C = 1.790 and 1.832 Å, \angle CoCCo = 78.8°, ring puckering 141°, and electron count 18-16: Werner, H.; Kolb, O.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* 1982, 240, 421. The ideas advanced here explain the distances in this dimer. The question of the lack of a metal-metal bond in palladium carbonyl dimers is explicitly discussed in a recent molecular orbital study: Kostić, N. M.; Fenske, R. F. *Inorg. Chem.* 1983, 22, 666.

to dimers with two π -acceptor bridging ligands. We have not analyzed triply bridged dimers, and the difference between dimers with π -acceptor and π -donor bridging ligands has already been noted by Hoffmann and co-workers.³

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada. Dr. F. Grein is thanked for extremely helpful discussions.

Additions and Corrections

1983, Volume 22

Katsuhiko Miyoshi, Noriko Katoda, and Hayami Yoneda*: Effect of the Nature of Other Ligands on the Rate of Nitrito-to-Nitro Linkage Isomerization of Octahedral Cobalt(III)-Amine Complexes in Aqueous Solution.

Page 1841. The structure of ω -[Co(en)(dien)(ONO)]²⁺ is wrongly depicted in Figure 4. The correct configuration is the same as that assumed by isomer III shown in Figure 1 of the third paper included in ref 23b.

Page 1841. In the last sentence: "having one more in-plane chelate ring adjacent to another in-plane ring" should read "having one more out-plane chelate ring cis to the in-plane ring".—Katsuhiko Miyoshi

Gerald E. Bossard, T. Adrian George,* Daniel B. Howell, Lenore M. Koczon, and Richard K. Lester: Reactions of Coordinated Dinitrogen. 12. Identification of Intermediates in the Conversion of Molybdenum-Bound Dinitrogen into Ammonia and Hydrazine. Factors Affecting the Ammonia-Forming Reaction.

Page 1969. In the second sentence of the seventh paragraph, **4B** appeared twice. In each case **4B** should have been **5**.—T. Adrian George