H, multiplet), 5.28 (C_5H_5, doublet, $J_{PH} = 1.2$ Hz), 5.65 (CH_2, multiplet) with relative intensities 1:3:5:4, respectively. ^{31}P NMR spectrum in $CHCl_3$: −223.4 ppm (singlet).

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)[\overline{POCH_2CH_2O}(OC_6H_5)]C_6H_5$ (7). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]C_6H_5$ (3.81 g, 7.80 mmol) and $C_6H_5O\overline{POCH_2CH_2O}$ (2.27 g, 12.4 mmol) in 100 ml of benzene was heated under reflux for 10 h. Solvent was removed on the rotary evaporator. The residue was dissolved in 9:1 petroleum ether/dichloromethane and was chromatographed on a 2.5 × 30 cm alumina column. The resulting three bands were successively eluted with the 9:1 mixture. The first band (pale yellow) contained $P(C_6H_5)_3$ and unreacted $C_6H_5O\overline{PCH_2CH_2O}$. An orange band eluted next. Concentration of the eluate on the rotary evaporator and subsequent filtration afforded 180 mg of unreacted $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]C_6H_5$. The product eluted as a large yellow band. Removal of solvent from the eluate on the rotary evaporator gave a yellow solid. Recrystallization at −10° from a mixture of ether and heptane gave 2.00 g of yellow crystalline product (66% yield based on unrecovered starting material), mp 74–75°. Anal. Calcd for $C_{20}H_{19}O_4PFe$: C, 58.56; H, 4.67; P, 7.55. Found: C, 58.68; H, 4.70; P, 7.34.

Infrared spectrum (cyclohexane): ν_{CO} 1953 cm^{-1}. ^1H NMR spectrum in $CDCl_3$: τ 2.83 (aromatic H, complex multiplet), 5.32 (C_5H_5, doublet, $J_{PH} = 0.9$ Hz), 6.29 (CH_2, multiplet) with relative intensities 10:5:4, respectively. ^{31}P NMR spectrum in $CHCl_3$: −194.5 ppm (singlet).

Acknowledgment (by R.P.S.) is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We are grateful to Professor W. A. G. Graham of the University of Alberta for providing us with the unpublished results cited in ref 29. Discussions with Professor Gilbert Gordon are gratefully acknowledged. We especially thank Mr. Samuel J. Wilkof for his expertise in synthesizing phenyl ethylenephosphite.

References and Notes

(1) (a) Miami University; (b) The Procter & Gamble Company, Miami Valley Laboratories.
(2) R. P. Stewart, Jr., J. J. Benedict, L. Isbrandt, and R. S. Ampulski, *Inorg. Chem.*, **14**, 2933 (1975), and references therein.
(3) R. J. McKinney, R. Hoxmeier, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3059 (1975), and references cited therein.
(4) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970).
(5) G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).
(6) M. Y. Darensbourg, D. J. Darensbourg, and D. Drew, *J. Organomet. Chem.*, **73**, C25 (1974).
(7) L. W. Gosser, *Inorg. Chem.*, **14**, 1453 (1975).
(8) W. H. Knoth and R. A. Schunn, *J. Am. Chem. Soc.*, **91**, 2400 (1969).
(9) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Am. Chem. Soc.*, **91**, 4990 (1969).
(10) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 639 (1970).
(11) M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J. Organomet. Chem.*, **40**, C 39 (1972).
(12) M. I. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1667 (1973).
(13) E. W. Ainscough, T. A. James, S. D. Robinson, and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 2384 (1974).
(14) E. K. Barefield and G. W. Parshall, *Inorg. Chem.*, 11, 964 (1972).
(15) M. A. Bennett and R. Charles, *Aust. J. Chem.*, **24**, 427 (1971).
(16) E. W. Ainscough, S. D. Robinson, and J. J. Levison, *J. Chem. Soc. A*, 3413 (1971).
(17) L. M. Haines and E. Singleton, *J. Organomet. Chem.*, **25**, C83 (1970).
(18) N. Ahmad, E. W. Ainscough, T. A. James, and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1151 (1973).
(19) For recent comprehensive reviews see (a) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, Chapter 4; (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 196–205.
(20) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972, p 476.
(21) R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, **2**, 15 (1964).
(22) A. N. Nesmeyanov, Yu. A. Chapovsky, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, **9**, 345 (1967).
(23) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).
(24) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).
(25) A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, 754, 860 (1972).
(26) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(27) We use the more general term *internal* metalation to include intramolecular formation of metal–carbon σ bonds to *alkyl* groups of coordinated phosphorus ligands. For relevant examples see ref 3–5, 24, 25.
(28) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
(29) R. P. Stewart, Jr., and W. A. G. Graham, unpublished observations.
(30) K. N. Scott, *J. Am. Chem. Soc.*, **94**, 8564 (1972).
(31) L. F. Farnell, and E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).
(32) H. C. Clark and J. E. H. Ward, *J. Am. Chem. Soc.*, **96**, 1741 (1974).
(33) B. E. Mann, *Adv. Organomet. Chem.*, **12**, 135 (1974).
(34) L. R. Isbrandt, R. K. Jensen, and L. Petrakis, *J. Magn. Reson.*, **12**, 143 (1973).
(35) Reference 19a, p 90.
(36) W. Keim, *J. Organomet. Chem.*, 14, 179 (1968).
(37) M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(38) S. A. Dias, A. W. Downs, and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 162 (1975).
(39) A. R. Garber, P. E. Garrou, G. E. Hartwell, M. J. Smas, J. R. Wilkinson, and L. J. Todd, *J. Organomet. Chem.*, **86**, 219 (1975).
(40) D. C. Ayres and H. N. Rydon, *J. Chem. Soc.*, 1109 (1957).
(41) A. N. Nesmeyanov, L. G. Makarova, and I. V. Polovyanyuk, *J. Organomet. Chem.*, **22**, 707 (1970).

Triple-Decker Sandwiches

Joseph W. Lauher, Mihai Elian, Richard H. Summerville, and Roald Hoffmann*

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received September 15, 1975*

Abstract: By making use of the frontier orbitals of MCp and $M(CO)_3$ fragments, the electronic structure of triple-decker sandwiches CpMCpMCp and $(CO)_3MCpM(CO)_3$ is analyzed. Two series of stable structures, containing 30 and 34 valence electrons, respectively, are predicted. The known $Ni_2Cp_3^+$ and $Co_2Cp_2(C_2B_3H_4R)$ triple deckers are representatives of these two series. There are important similarities between these compounds and normal triply CO bridged dimers of the $Fe_2(CO)_9$ type. The theoretical analysis is extended to types such as $(CH)_nM(CO)_3M(CH)_n$ and $(CO)_3M(CH)_nM(CO)_3$, suggesting a number of potential synthetic goals.

Bis(η^5-cyclopentadienyl) transition metal complexes, MCp_2 (**1**), have been known for about 25 years. There is a vast chemistry of these metallocenes or sandwich compounds. More recently Werner and Salzer prepared for the first time a triple-decker sandwich compound, the tris(η^5-cyclopentadienyl)dinickel cation,[1] $Ni_2Cp_3^+$ (**2**). The structure of this cation was determined[2] and shows three parallel Cp ligands with the two nickel atoms sandwiched in-between. The possible existence of such a species was first suggested by Schumacher and Taubenest,[3] who studied the mass spectrum of nickelocene.

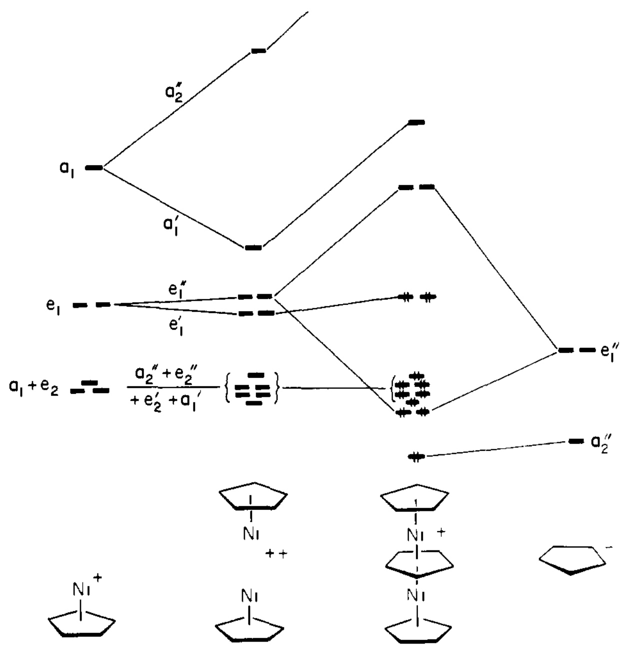
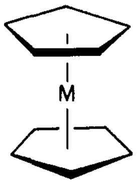
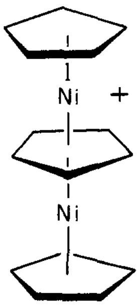


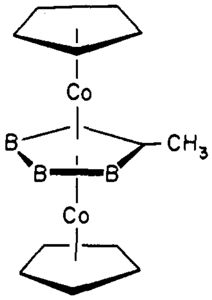
Figure 1. Interaction diagram for the frontier orbitals of $Ni_2Cp_3^+$. At left two $NiCp^+$ fragments are combined to a weakly interacting $Ni_2Cp_2^{2+}$. This is then allowed to mix with the central Cp^-.



1



2



3

They found that the $Ni_2Cp_3^+$ cation was formed by an ion molecule reaction and correctly predicted the triple-decker structure.

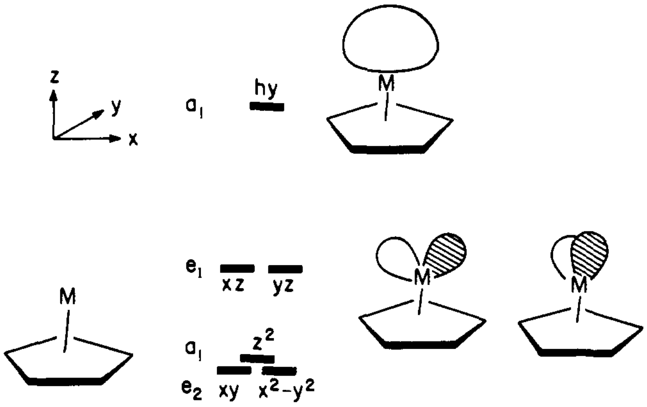
Triple-decker complexes of cobalt are also known. These stable compounds have as the middle ring not a Cp ligand but a carborane ring. The three compounds prepared are $Co_2(C_5H_5)_2(1,2\text{-}C_2B_3H_5)$, $Co_2(C_5H_5)_2(1,3\text{-}C_2B_3H_5)$, and the methyl substituted complex, $Co_2(C_5H_5)_2(3\text{-}CH_3\text{-}2,3\text{-}C_2B_3H_4)$ (**3**), the crystal structure of which was determined.[4]

We present here a molecular orbital analysis of these unique triple-decker sandwich compounds, and relate their electronic structures to those of more conventional dimeric complexes. Our study suggests several series of interesting compounds, potentially stable, which remain to be synthesized.

The Fragment Analysis and the Ni and Co Triple Deckers

The electronic structure of the triple-decker CpM-Cp-MCp may be approached from a number of different viewpoints. We have found convenient a fragment analysis[5] based on an obvious partitioning of the molecule. The valence orbitals of the MCp and isolated Cp fragments are well known,[5a,d] and in the reassembly of the molecule symmetry is a powerful simplifier. The qualitative conclusions we present here stem from extended Huckel calculations, described in the Appendix.

The characteristic features of the MCp fragment are summarized in **4**. There are three relatively low-lying orbitals, $a_1 + e_2$, fully occupied in a low-spin d^6 configuration and composed primarily of metal z^2, xy, and $x^2 - y^2$. At higher energy is an e_1 set which is mainly metal xz and yz, hybridized to some extent with x and y to give these orbitals a shape extending away from the cyclopentadienyl ligand. Still higher in energy lies an a_1 orbital, denoted as "hy", which is a hybrid of metal s and z, again pointing away from the Cp. The higher $a + e_1$ set will bear the brunt of interaction once this fragment is allowed to approach another molecule, so that an acquaintance with their rough shape (see **4**) and energy is important.

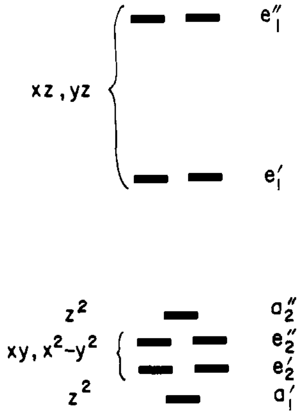


4

For $Ni_2Cp_3^+$ the natural partitioning is into $CpNi^+\cdots Cp^-\cdots NiCp^+$. The interaction diagram of Figure 1 was constructed from an extended Huckel calculation on an idealized D_{5h} geometry in which the distance between the Ni atoms and the outer and inner Cp ring planes was taken as 1.73 and 1.79 Å, respectively. The left side of the figure shows the interaction of the two $NiCp^+$ fragments in the absence of the central cyclopentadienyl ring. At a Ni-Ni separation of 3.58 Å the level splittings are small except for the a_1' and a_2'' levels derived from the hy orbital of MCp^+. The s and z orbitals which make up this hybrid are diffuse and overlap significantly even at such a long metal-metal distance.

On the right of Figure 1 are shown the donor π orbitals of the bridging Cp^- ligand, a_2'' and e_1''. These interact strongly with corresponding symmetry combinations derived from the NiCp hy and xz, yz orbitals. The nonbonding NiCp set of z^2, xy, and $x^2 - y^2$ remains nonbonding and is just doubled by the presence of the two NiCp fragments. Our calculations also show that there are important interactions of the σ orbitals of the central Cp^- ligand with appropriate symmetry orbitals of the NiCp caps. The σ orbitals of the Cp^- which are involved are not shown in Figure 1, but their effect can be seen in the destabilization of the a_1' and e_1' levels.

The basic level pattern that emerges, and that is characteristic of all these complexes, is shown below in **5**. There are



5

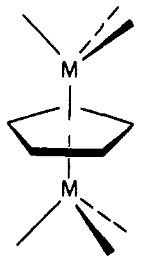
six filled low-lying orbitals and two high-lying e sets. The higher of these, e_1'', is strictly antibonding, too high for occupancy. The lower e_1' set is slightly antibonding with the outer rings and essentially nonbonding with the bridging Cp. This e_1' orbital set is occupied with four electrons in $Ni_2Cp_3^+$.

The cobalt triple deckers have unusual carborane rings as the central bridging ligand. These rings, two isomers of $C_2B_3H_5^{4-}$, do not have an independent existence. However, they are isoelectronic with $C_5H_5^-$ and given theoretical license we may view them as we did the Cp rings in $Ni_2Cp_3^+$. The difference that we must take into account is that with the high formal negative charge on the carborane ligand there would be expected strong donation of electron density to the cobalt atoms. The effect of this would be a greater d level splitting. Both high-lying e sets should be considerably destabilized. In fact the cobalt triple deckers are not isoelectronic with $Ni_2Cp_3^+$ but contain four less electrons. The e_1' orbitals are not occupied in the Co case.

The electron counting in these complexes may be accomplished in a number of ways. In $Ni_2Cp_3^+$ we have 3 six-electron donating Cp^- ligands and 16 d electrons on the two metal atoms, giving a total of 34 electrons. Our analysis indicates that the e_1' orbitals occupied in this system are not essential for bonding, and suggests that a family of 30 electron complexes should also be endowed with thermodynamic and kinetic stability. The $Co_2Cp_2(C_2B_3H_4R)$ structures in fact can be viewed as belonging to this second family.

Still another point of view places these molecules within the general context of metal and main group polyhedral clusters.[6,7] A $CoCp^{2+}$ fragment, needed for assembly of the $Co_2Cp_2(C_2B_3H_4R)$ series, is analogous to CH^{3+} or BH^{2+}. As suggested by Grimes and co-workers[4] the Co triple deckers are analogous to the known pentagonal bipyramid $B_7H_7^{2-}$. It is interesting to note that the Ni triple deckers, with four electrons more, are loosely analogous to $B_7H_7^{6-}$ or $C_7H_7^+$. The available calculations[8] indicate no features of stability for pentagonal bipyramids with ten electron pairs.

In addition to the M_2Cp_3 system we have carried out a series of calculations on $(CO)_3M$-Cp-$M(CO)_3$ (**6**). The MCp and $M(CO)_3$ fragments can be termed *isolobal*, by which neologism we mean that the number, symmetry properties, shapes, and energies of their frontier orbitals are approximately the same. We do not imply that the orbitals are identical nor isoelectronic, but only that they are similar in these properties. That similarity confers upon the fragments analogous bonding capabilities and a corrolary pattern of replacement in real and hypothetical molecules.



6

The orbital scheme for an $M(CO)_3$ fragment is similar to **4.** There are of course minor differences between the frontier orbitals, differences in energy, delocalization to the ligands, and hybridization.[5d] A final level pattern similar to **5** emerges, except that e_1' is at somewhat higher energy. Once again two families of structures are in principle possible, with 30 or 34 electrons, respectively. Representatives of the two families would be $(CO)_3MnCpMn(CO)_3^+$ and $(CO)_3CoCpCo(CO)_3^+$. An analysis of the entire family of $(CO)_3M$-cyclopolyene-$M(CO)_3$ and CpM-cyclopolyene-MCp structures leaves us with the impression that level scheme **5** is quite general and that there is considerable variation in the energy of the crucial e_1' orbitals. We also note that an analysis of these structures has been carried out earlier by Brown.[9]

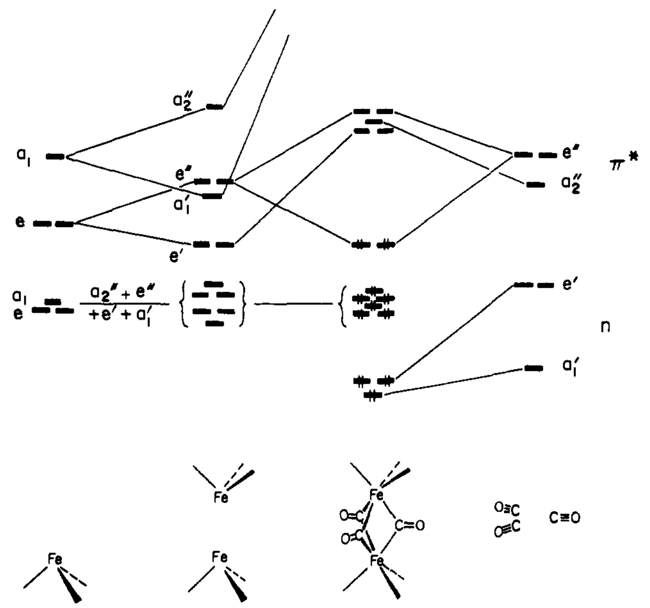
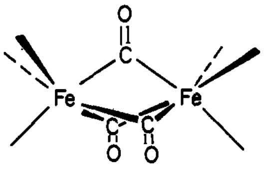


Figure 2. Interaction diagram for the frontier orbitals of $Fe_2(CO)_9$. At left two $Fe(CO)_3$ fragments are combined, held in the same geometry that they assume in the final $Fe_2(CO)_9$ structure. Then the $Fe_2(CO)_6$ composite is mixed with the three bridging CO's at right.

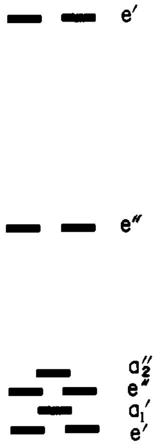
A Molecular Orbital Scheme for $Fe_2(CO)_9$ and Its Connection to the Inverse Sandwich Problem

Let us now analyze, in a manner similar to that used for the triple-decker structures, a more conventional bridged metal dimer. $Fe_2(CO)_9$ is an ideal species for this purpose. We partition the molecule into two $Fe(CO)_3$ fragments, 2.52 Å apart, bridged by a set of three CO molecules. Figure 2 shows the assembly of the molecule. The $Fe(CO)_3$ fragment orbitals are well known,[5a] and conform to pattern **4.** The metal atoms are closer together than in the M_2Cp_3, so that there is at left of Figure 2 a greater e′-e″ splitting than was found in Figure 1. In the D_{3h} symmetry the three bridging CO's bring donor orbitals of $a_1' + e'$ and acceptor orbitals of $a_1' + e' + a_2'' + e''$ symmetry. The three donor orbitals interact in typical fashion with the $(CO)_3Fe\cdots Fe(CO)_3$ framework orbitals. The high-lying framework e″ orbital is stabilized by the CO π* e″ combination. And just as in the M_2Cp_3 story the six nonbonding orbitals of the two metal fragments remain approximately constant in energy.



7

The essential d level scheme is shown in **8,** and should be compared with the triple-decker pattern **5.** A striking similarity is observed. Both systems have six low-lying filled d orbitals and two higher lying e sets. Both are 34 electron systems. The difference between the two lies in the inversion of the two high lying e sets. In the Cp compound the e′ set is lower and occu-

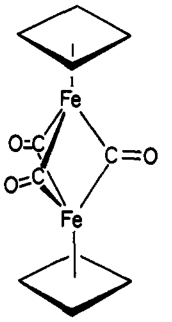


8

pied, while in $Fe_2(CO)_9$ it is the e″ set which is occupied. The inversion follows from the fact that the prime donor orbital of the Cp ligand is $e_1″$, while the corresponding $(CO)_3$ donor is e′. An important additional difference, mentioned above, is the presence of an e″ orbital among the carbonyl π^* levels. There is no back-bonding counterpart in the Cp dimer.

An amusing sidelight to this discussion is to point out that, while many ascribe a metal-metal bond to $Fe_2(CO)_9$ (Fe-Fe distance, 2.52 Å), few would ascribe a metal-metal bond to $Ni_2Cp_3^+$ (Ni-Ni, 3.6 Å). And yet it is in $Ni_2Cp_3^+$ that electrons occupy the symmetric e′ set, *bonding* between the metals, while in $Fe_2(CO)_9$ the corresponding electrons are in an antisymmetric e″ set, *antibonding* between the metals. The answer to this paradox is that in a molecular orbital scheme one cannot so readily assign specific metal-metal bonds. In $Ni_2Cp_3^+$ the $e_1′$ set is in fact essentially nonbonding between the metal atoms, even if it has the right phase for direct bonding. In $Fe_2(CO)_9$ the occupied e″ set may be metal-metal antibonding, but more importantly it contributes to the overall stability of the complex by being strongly metal-bridging CO bonding. In a separate publication we will attempt to untangle the various factors which determine the geometries of conventional bridged metal dimer systems.[10]

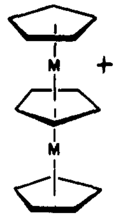
In light of the $Fe_2(CO)_9$-M_2Cp_3 analogy an obvious question is whether there are any 30 electron dimers with three bridging CO ligands. There appear to be none directly analogous to $Fe_2(CO)_9$, but there is an interesting related structure $(C_4Ph_4)Fe(CO)_3Fe(C_4Ph_4)$,[11] **9**. Each $Fe(C_4R_4)$ fragment is isolobal with $Fe(CO)_3$, but carries two less electrons.[5d] The interaction diagram for **9** is thus very similar to that for $Fe_2(CO)_9$, **8**, but with the significant difference that the levels which correspond to the filled e″ set in **8** are empty in the cyclobutadiene dimer. Since these two levels are antibonding between the metals there is a considerable shortening of the Fe-Fe bond length, now 2.2 Å. An interesting synthetic goal would be the 34 electron complex $Ni_2(CO)_3(C_4R_4)_2$ which would be expected to have a longer metal-metal bond distance.



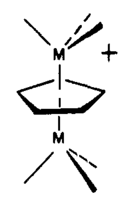
9

Missing Molecules and Near Misses

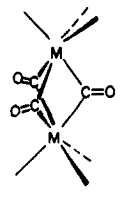
The preceding sections have delineated the electronic structure of triple-decker sandwiches and linked them to conventional bridged dimers. A central feature of their common level scheme is that closed shell structures are anticipated for both 30 and 34 electron dimers. Utilizing the isolobal character of the MCp and $M(CO)_3$ fragments, one can write the following series of analogous complexes. Molecules **10a** and **12a** are known. $Fe_2Cp_3^+$, **10b**, has been seen in mass spectrometric studies.[2,12] **12b**, $Cr_2(CO)_9$, may be a poor prospect because of the stability of $Cr(CO)_6$, but perhaps might be observable in matrix isolation experiments. **13a** and **13b** appear to be reasonable possibilities. A close nickel analogue to **13a** is known, $Ni_2(CO)_2Cp_2$.[13] The manganese complex **13b** would be similar to the iron cyclobutadiene dimer previously discussed, **9**. More unprecedented would be the synthesis of the "inverse sandwich" structures **11a** and **11b**.



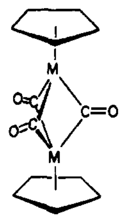
10a Ni
10b Fe



11a Co
11b Mn

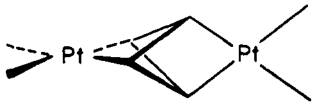


12a Fe
12b Cr



13a Co
13b Mn

It should be noted that there are a number of analogous series with cyclopolyene or cyclopolyenyl rings of various sizes taking the place of the cyclopentadienyl ring in structures **10–13**. The electronic requirements of such structures are easily analyzed with the fragment methodology. A further departure still allows one to write down structures such as **14**, where the puckering of the central ring is only a speculation.

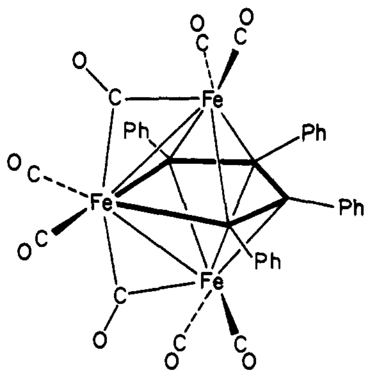


14

Next we would like to mention some instances in which triple-decker or inverse sandwich structures have been invoked or are reasonable structural alternatives to think about, as well as some cases where molecular structures approach a triple-decker sandwich geometry.

The term "triple decker" was introduced by Piper, Cotton, and Wilkinson[14] in the context of postulated structures for $CpMo(CO)_5MoCp$ and $CpW(CO)_6WCp$, whose actual structures of course turned out to be what are now familiar metal-metal bonded types. Triple-decker structures with cyclobutadiene as a central bridge were postulated by Krüerke and Hübel[15] for compounds of the composition $Co_{2n}Hg_n(CO)_{4n+4}(PhC_2H)_{2n-2}$, $n = 2, 3$, but to our knowledge no structural proof is available for these compounds. Triple-decker structures have been logically invoked as way-points in the characteristic arene exchange reactions of arene-metal-tricarbonyl complexes.[16,17] Perhaps not unrelated to the question of the possible stability of triple deckers is the ability of sandwich complexes to form charge-transfer complexes with aromatic acceptors.[18,19] The crystal structures of two such complexes have been determined[20,21]—they resemble normal arene donor-acceptor complexes.

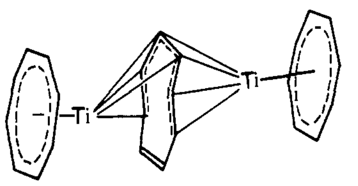
An interesting structure of some complexity is that of $Fe_3(CO)_8(CPh)_4$[22] shown in **15**. It approaches a triple-decker



15

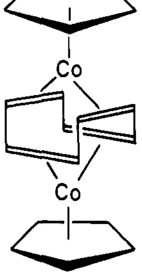
structure, and could just as well be classified as an Fe_3C_4 mixed metal-main group cluster.

A structure close to a triple decker is that of tris(cyclooctatetraene)dititanium (**16**).[23] Each Ti is close to four carbon atoms, and two of these are shared by the two Ti atoms. We note that a symmetrical structure, octahapto on the central ring, of COT-Ti-COT-Ti-COT may easily be shown to be characterizied by a half-filled degenerate orbital. Slippage out of the most symmetrical structure is bound to occur, but why the particular coordination geometry that is observed is adopted awaits an explanation.



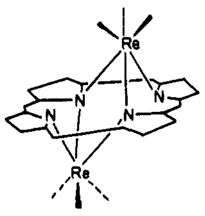
16

Another cyclooctatetraene complex, Cp_2Co_2COT, adopts the expected structure **17**,[24] in which each Co achieves an 18-electron configuration by coordinating with two double bonds of the cyclooctatetraene. It is interesting that a true triple-decker structure, with both cobalt atoms coordinating to all eight carbons of the central ring, is allowed for two electrons more than in the original compound. This is a 38-electron system, with the extra four electrons occupying an e_2 orbital of the cyclooctatetraene. For large rings entering into the triple-decker bonding mode one has to modify the electron counting to include these additional e_2 orbitals.



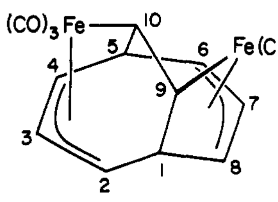
17

Returning to near triple-decker structures, we next note the interesting porphyrin-$(M(CO)_3)_2$ complexes, M = Re, Ti, explored by Tsutsui and co-workers.[25] In the unusual structure that these possess, **18**, each metal atom is complexed to three pyrrole nitrogens, two of which are common to both metal coordination spheres.



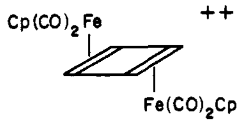
18

One of many interesting products of the interaction of bullvalene with iron carbonyls is the molecule **19**.[26] The compound is fluxional, with $\Delta G^{\ddagger}$ for H_2-H_4 interchange of 16.0 kcal/mol.[26] We see no special stabilizing features in a possible symmetrical transition state for concerted $Fe(CO)_3$ shift from C_9 to C_{10}.



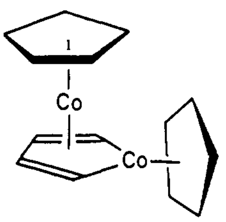
19

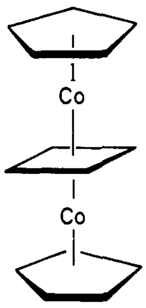
A novel di-η^2-cyclobutadiene structure has been assigned to compound **20**.[27] A symmetrical triple-decker structure with both iron atoms coordinated to all four cyclobutadiene carbons is likely to be Jahn-Teller unstable. A concerted switch of $Fe(CO)_2Cp$ groups to the other double bond is a forbidden reaction. If the $Fe(CO)_2Cp$ groups migrate, they should do so through monohapto intermediates around the cyclobutadiene periphery.



20

$Co_2Cp_2C_4H_4$ has been synthesized by a photochemical reaction of photo-α-pyrone with $CpCo(CO)_2$.[28] Its structure is **21**.[28,29] The exchange of Cp rings is intramolecular and proceeds with an activation energy of 25.8 kcal/mol. One possible exchange mechanism, through the triple-decker waypoint **22**, could be eliminated since the cyclobutadiene protons maintain their identity while the Cp rings interchange. This is consistent with **22** not being a stabilized closed shell structure. Two more electrons are required.





21 **22**

Acknowledgment. Our work was supported by the National Science Foundation, Grant GP-28137, and the Advanced Research Projects Agency through the Materials Science

Table I. Extended Hückel Parameters

		Exponents[a]	
Orbital	H_{ii}	ζ_1	ζ_2
Mn 4s	−9.75	0.97	
Mn 4p	−5.89	0.97	
Mn 3d	−11.67	5.15 (0.5139)	1.70 (0.6929)
Fe 4s	−9.91	1.575	
Fe 4p	−5.07	0.975	
Fe 3d	−12.63	5.35 (0.5366)	1.80 (0.6678)
Co 4s	−10.29	1.70	
Co 4p	−6.11	1.05	
Co 3d	−12.84	5.55 (0.5551)	1.90 (0.6461)
Ni 4s	−10.95	1.825	
Ni 4p	−6.27	1.125	
Ni 3d	−14.17	5.75 (0.5683)	2.00 (0.6292)
C 2s	−21.40	1.625	
C 2p	−11.40	1.625	
H 1s	−13.60	1.3	
O 2s	−32.3	2.275	
O 2p	−14.8	2.275	

[a] Two Slater exponents are listed for the 3d functions. Each is followed in parentheses by the coefficient in the double zeta expansion.

Center at Cornell University. We are also grateful to the Committee on International Exchange of Persons (Senior Fulbright-Hays Program) which made possible the stay of M.E. (from the Institute of Organic Chemistry, Bucharest, Romania) at Cornell University. We also appreciate the comments and discussion of our research group and D. M. P. Mingos and the communication of some results prior to publication by R. N. Grimes.

Appendix

All the calculations were of the extended Hückel type.[30] Parameters used previously[30] for carbon, hydrogen, and oxygen were kept fixed during charge iterations. Metal orbital exponents were taken from the work of Richardson et al.[31] Charge iterations with an assumed quadratic charge dependence of metal H_{ii}'s[32] were performed on suitable model compounds: iron pentacarbonyl, Fe-C 1.85 Å, C-O 1.15 Å; cobalticinium ion, Co-C 2.155 Å, C-C 1.41 Å, C-H 1.10 Å; nickelocene, Ni-C 2.16 Å, C-C 1.41 Å, C-H 1.1 Å. Parameters for manganese were taken from a previous iteration on cyclopentadienyl manganese tricarbonyl.[5] Calculations on the dimeric molecules were performed by the usual noniterative extended Hückel method using metal H_{ii}'s obtained in the charge iterations. All parameters for these calculations are listed in Table I.

References and Notes

(1) (a) H. Werner and A. Salzer, *Synth. Inorg. Met.-Org. Chem.*, **2**, 239 (1972); (b) A. Salzer and H. Werner, *Angew. Chem.*, **84**, 949 (1972).
(2) E. Dubler, M. Textor, H.-R. Oswald, and A. Salzer, *Angew. Chem.*, **86**, 125 (1974).
(3) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **47**, 1525 (1964); $Fe_2Cp_3^+$ and $FeNiCp_3^+$ were also detected in this work.
(4) (a) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Am. Chem. Soc.*, **95**, 3046 (1973); R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974). (b) The crystal structure of the methyl-substituted 1,3-isomer has also been determined: W. T. Robinson and R. N. Grimes, *Inorg. Chem.*, **14**, 3056 (1975). (c) Several other metallocarboranes of the triple-decker class have been prepared, including $(C_2B_3H_7)Co(C_2B_3H_5)Co(C_5H_5)$: R. N. Grimes, private communication.
(5) For applications see (a) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975); (b) R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, **98**, 598 (1976); (c) J. W. Lauher and R. Hoffmann, *ibid.*, **98**, 0000 (1976); (d) M. M.-L. Chen, D. M. P. Mingos, M. Elian, and R. Hoffmann, *ibid.*, in press.
(6) D. M. P. Mingos, *Nature* (*London*), *Phys. Sci.*, **236**, 99 (1972).
(7) K. Wade, *Chem. Commun.*, 792 (1971); *Inorg. Nucl. Chem. Lett.*, **8**, 559, 563 (1972); "Electron Deficient Compounds", Nelson, London, 1971.
(8) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); E. L. Muetterties and B. Beier, *Bull. Soc. Chim. Belg.*, **84**, 397 (1975).
(9) D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39, 49 (1959).
(10) R. H. Summerville and R. Hoffmann, to be submitted for publication.
(11) The crystal structure is actually that of a di-*tert*-butyldiphenyl derivative: S.-I. Murahashi, T. Mizoguchi, T. Hosokawa, I. Moritani, Y. Kai, M. Kohara, N. Yasuoka, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 563 (1974).
(12) For other mass spectrometric studies in which triple-decker structures were proposed see J. Müller and K. Fenderl, *Chem. Ber.*, **103**, 3141 (1970); **104**, 2199 (1971); P. E. Gaivoronskii and N. V. Larin, *Usp. Khim.*, **43**, 1035 (1974).
(13) Synthesis: E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1963).Structure: J. P. Nice, Ph.D. Thesis, University of Manchester, 1966.
(14) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).
(15) E. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961).
(16) H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, "Benzenoid-Metal Complexes", Ronald Press Co., New York, N.Y., 1966.
(17) W. Strohmeier and R. Müller, *Z. Phys. Chem.* (*Frankfurt am Main*), **40**, 85 (1964); W. Strohmeier and H. Mittnacht, *ibid.*, **29**, 339 (1961), and references therein.
(18) M. Rosenblum, R. W. Fish, and C. Bennett, *J. Am. Chem. Soc.*, **86**, 5166 (1964).
(19) H. Kobayashi, M. Kobayashi, and Y. Kaizu, *Bull. Chem. Soc. Jpn.*, **46**, 3109 (1973); **48**, 1222 (1975).
(20) O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 822 (1966).
(21) E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Am. Chem. Soc.*, **89**, 4540 (1967).
(22) R. P. Dodge and V. Schomaker, *J. Organomet. Chem.*, **3**, 274 (1965).
(23) (a) H. Breil and G. Wilke, *Angew. Chem.*, **78**, 942 (1966); (b) H. Dierks and H. Dietrich, *Acta Crystallogr., Sect. B*, **24**, 58 (1968).
(24) Synthesis: H. P. Fritz and H. Keller, *Z. Naturforsch. B*, **16**, 348 (1961); E. O. Fischer, H. P. Fritz and C. G. Kreiter, *Chem. Ber.*, **96**, 2632 (1963). Structure: E. Paulus, W. Hoppe and R. Huber, *Naturwissenschaften*, **54**, 67 (1967).
(25) D. Cullen, E. Meyer, T. S. Srivastava, and M. Tsutsui, *J. Am. Chem. Soc.*, **94**, 7603 (1972); M. Tsutsui, C. P. Hrung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, and E. F. Meyer, Jr., *ibid.*, **97**, 3952 (1975). See also M. F. Hudson and K. M. Smith, *J. Chem. Soc., Chem. Commun.*, 515 (1973); *Tetrahedron Lett.*, 2223 (1974); Z. Yoshida, H. Ogoshi, T. Omura, E. Watanabe, and T. Kurosaki, *Tetrahedron Lett.*, 1077 (1972); A. Takenaka, Y. Sasada, T. Omura, H. Ogoshi, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 792 (1973).
(26) R. Aumann, *Angew. Chem.*, **83**, 176 (1971); R. Aumann, *Chem. Ber.*, **108**, 1974 (1975). The crystal structure of **18** has been determined by I. C. Paul and C. C. Chiang, University of Illinois, private communication.
(27) A. Sanders and W. P. Giering, *J. Am. Chem. Soc.*, **96**, 5248 (1974).
(28) M. Rosenblum, B. North, D. Wells, and W. P. Giering, *J. Am. Chem. Soc.*, **94**, 1239 (1972). See also R. S. Dickson and H. P. Kirsch, *Aust. J. Chem.*, **27**, 61 (1974).
(29) O. S. Mills, cited in footnote 16 of ref 28.
(30) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
(31) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *ibid.*, **36**, 1057 (1962).
(32) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).