References and Notes

(1) For reviews of the Fischer-Tropsch reaction see (a) H. H. Storch, N. Golumbic, and R. B. Anderson, "The Fischer-Tropsch and Related Synthesis", Wiley, New York, N.Y., 1951; (b) P. H. Emmett, Ed., "Catalysis", Vol. 4, Reinhold, New York, N.Y., 1956.
(2) M. A. Vannice, *J. Catal.*, **37**, 449, 462 (1975).
(3) I. Howard-Smith and G. J. Werner, "Coal Conversion Technology 1976", Chemical Process Technology Review No. 66, Noyes Data Corporation, Park Ridge, N.J., 1976.
(4) While carbonylation reactions of alkyl metal compounds are well known,[5] there is no direct evidence that the substitution reactions of metal carbonyl hydrides give formyl complexes or proceed via formyl intermediates[6a] although the intermediacy of metal formyl complexes has been considered.[6b,c]
(5) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 88 (1973).
(6) (a) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 947 (1975); (b) A. Berry and T. L. Brown, *J. Organomet. Chem.*, 33, C67 (1971); (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967 p 555.
(7) J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973).
(8) W. Siegl, *J. Organomet. Chem.*, **92**, 321 (1975).
(9) J. Chatt, G. Leigh, and N. Thankarajan, *J. Organomet. Chem.*, **29**, 105 (1971).
(10) M. Y. Darensbourg, *J. Organomet. Chem.*, submitted for publication.
(11) M: Churchill, S. W.-Y. Ni Chang, M. Berch, and A. Davison, *J. Chem. Soc., Chem. Commun.*, 691 (1973).
(12) R. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).
(13) (a) H. C. Brown and E. Mead, *J. Am. Chem. Soc.*, **75**, 6263 (1953); (b) H. C. Brown, E. Mead, and C. Shoaf, *J. Am. chem. Soc.*, **78**, 3616 (1956).
(14) Yields are determined by integration of the characteristic formyl proton resonance with respect to a weighed amount of added toluene.
(15) Detailed procedures for these preparations are included as supplementary material.
(16) Ir (THF) 2690 (w), 2510 (w), 2018 (w), 1930 (s), 1902 (vs), and 1607 (s) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 7.44–8.04 (m, 30 H, C_6H_5); 14.95 (s, 1 H, FeCHO). ^{13}C NMR (acetone-d_6) δ 129.8, 130.8, 131.5, 132.5, 133.3, 134.4 (C_6H_5); 221.1 (metal carbonyl), 270.5 (formyl carbon).
(17) Formaldehyde was isolated as the dimedone derivative and characterized by mass spectroscopy, M$^+$ 292.
(18) Ir spectrum of $Cr(CO)_6$ + Na$^+$ $HB(OCH_3)_3^-$ in THF: 2021 (w), 1903 (s), 1888 (s), 1838 (m) cm^{-1}, in addition to frequencies for $Cr(CO)_6$.
(19) We have found, by using identical methods, no evidence for formation of metal formyl compounds from $Mo(CO)_6$, $C_5H_5Mn(CO)_3$, $C_5H_5Fe(CO)(PPh_3)Br$, $(CO)_3Fe(PPh_3)_2$, and (p-xylene)$Cr(CO)_3$.
(20) C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).
(21) Anal. Calcd for $C_{30}H_{36}FeNO_7P$: C, 59.12; H, 5.95; Fe, 9.16; N, 2.30; P, 5.08. Found: C, 58.37; H, 6.05; Fe, 9.66; N, 2.02; P, 4.90.
(22) This assignment is based on the analogous assignment made by Collman.[7]
(23) For the analysis of the ir spectra of bis-substituted iron carbonyls see (a) J. Tripathi and M. Bigorgne, *J. Organomet. Chem.*, **9**, 307 (1967); (b) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

Charles P. Casey,* Stephen M. Neumann

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 7, 1976

A New Structural Type for $M_3(CO)_{12}$ Molecules and Their Derivatives. The Molecular Structure of $Ru_3(CO)_{10}$(1,2-diazine)

Sir:

We have previously called attention to the extreme structural variability of trinuclear metal carbonyl molecules,[1] such as $Fe_3(CO)_{12}$,[2,3] (η^5-$C_5H_5)_3Co_3(CO)_3$,[4] and the related (η^5-$C_5H_5)_3Rh_3(CO)_3$, under the influence of thermal energy, environment, and, more drastically, replacement of one or more CO ligands by other ligands. There are comparable examples among dinuclear species, e.g., (η^5-$C_5H_5)_2Fe_2(CO)_4$,[5] $Co_2(CO)_8$,[6,7] and $Fe_2(CO)_7$(dpy).[8]

We wish to report here some recent work which bears importantly, and interestingly, on this point. It is well known that the solid state structure of $Fe_3(CO)_{12}$ has two unsymmetrical bridges on one edge of the Fe_3 triangle[9,10] while that of $Ru_3(CO)_{12}$ is of D_{3h} symmetry and has no bridges.[11] It is also known that $Fe_3(CO)_{12}$ undergoes CO scrambling with extreme ease[3] and is an example, par excellence, of that class of easily deformable molecules which we have proposed to call *fictile molecules.*[4] $Ru_3(CO)_{12}$, on the other hand, though not fictile (ir spectrum normal in solution) is also readily fluxional, having only one ^{13}C resonance line at the lowest temperature (−100 °C) studied.[12]

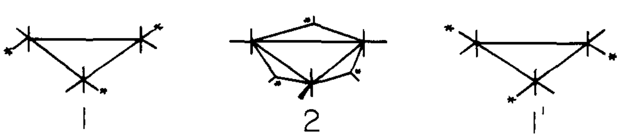


Figure 1. A plausible but undetected pathway for partial CO scrambling in an $M_3(CO)_{12}$ molecule of the $Ru_3(CO)_{12}$ type.

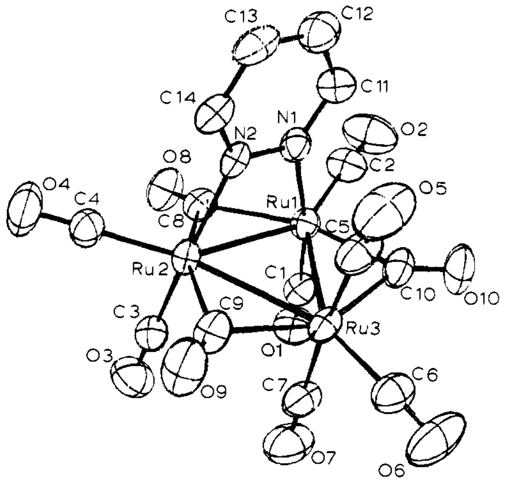


Figure 2. The molecular structure of $Ru_3(CO)_{10}(1,2\text{-}C_4H_4N_2)$. Atoms are represented by thermal vibration ellipsoids at the 50% level.

We have previously proposed[10] a mechanism for CO scrambling in $Fe_3(CO)_{12}$ that involves concerted rotatory motions of CO's on adjacent iron atoms in such a way that a pair of CO bridges is temporarily established across the bond between those two iron atoms. As the proposed process is carried forward, and repeated on the other edges of the Fe_3 triangle, all CO groups are caused to travel over the entire Fe_3 triangle and to have time-average equivalence. It is important to realize, however, that even though this process can account, by itself, for *all* the spectroscopic observations[3] on $Fe_3(CO)_{12}$, one or more other, unperceived, processes, whose spectral effects are masked by the main process may also occur. The unperceived process (or processes) would involve some structurally different intermediate.[13] In the present case, one such process might be that shown in Figure 1, where the intermediate, **2**, has a bridging CO group on each edge and overall D_{3h} symmetry.[17] The process shown in Figure 1 cannot, of course, by itself account for the complete scrambling of CO groups; obviously, it scrambles only half of them. However, it is structurally a very plausible process and may well be occurring, even though its effects might be entirely masked by those of the more extensive scrambling process discussed above.

One form of evidence for the plausibility of any such structure as **2** is the actual observation of it, in slightly modified form, in a closely related system. We now report that sort of evidence for **2**. The reaction of pyridazine (1,2-diazine) with $Ru_3(CO)_{12}$ under appropriate conditions gives a deep maroon crystalline compound of stoichiometry $Ru_3(CO)_{10}(C_4H_4N_2)$. The structure, determined by standard x-ray crystallographic procedures,[18] is shown in Figure 2. Some important bond lengths are given in Table I.

The structure can be thought of as derived from **2** by replacement of two terminal CO groups on Ru1 and Ru2 by the pyridazine nitrogen atoms. As a result of the short N–N distance and preferred orientation of these nitrogen lone pairs, there is a slight tilting of the coordination polyhedra of Ru1 and Ru2 the most notable effects of which are that the CO

Table I. Selected Bond Lengths in $(C_4H_4N_2)Ru_3(CO)_{10}$[a]

Ru1-Ru2	2.743 (4)	Ru2-C8	2.16 (3)
Ru2-Ru3	2.859 (4)	Ru2-C9	2.06 (3)
Ru1-Ru3	2.857 (4)	Ru3-C9	2.15 (3)
Ru-C (av)	1.88[b]	Ru1-C10	2.07 (3)
Ru1-C8	2.08 (3)	Ru3-C10	2.20 (3)

[a] Bond lengths in Å. [b] Terminal carbonyls.

groups trans to the N atoms are not parallel and the bridging CO group, C8O8, is tilted out of the Ru_3 plane. Also Ru1-Ru2 is ~0.12 Å shorter than the other two Ru-Ru distances, which differ negligibly from those[11] in $Ru_3(CO)_{12}$ itself (2.849, 2.859, 2.837, each ±0.006). The expected mirror plane through Ru3 and perpendicularly bisecting the Ru1-Ru2 bond is violated by asymmetry in the bridging CO groups, for each of which the Ru-C distances differ by an average of 0.10 Å. The pattern of these deviations (both bonds to Ru1 are short, both to Ru3 are long) is inconsistent with the potential mirror symmetry nor does it seem to have any rationale in terms of electronic factors, as does the occurrence of unsymmetrical bridges in certain other cases.[1] Tentatively, we regard the asymmetry of the bridges as being at least partly a result of packing forces. It is possible that in the ideal structure (i.e., the one determined only by internal factors) the two Ru3-Ru1 and Ru3-Ru2 bridges might have the intrinsic asymmetry observed due to the different electron densities and different steric factors at Ru1 and Ru2 as compared to Ru3. However, the asymmetry of the bridge across Ru1 and Ru2 would then have to be attributed to extrinsic factors such as intermolecular contacts. One must, then, also recognize that if one such distortion could be of extrinsic origin, then so might all three. The molecule appears to retain its basic structure, perhaps undistorted, in solution since the infrared spectrum in THF shows at least five terminal bands (2083, 2035, 2003, 1998, and 1964 cm^{-1}) and a broad band at 1820 cm^{-1} with intensity ratios consistent with terminal and bridging groups in a 7:3 ratio. Further studies, especially by NMR are being conducted.[19]

References and Notes

(1) F. A. Cotton, *Prog. Inorg. Chem.*, **21**, 1 (1976).

(2) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 5070 (1974).

(3) F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).

(4) F. A. Cotton and J. D. Jamerson, *J. Am. Chem. Soc.*, **98**, 1273 (1976).

(5) Cf. R. D. Adams and F. A. Cotton in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, Chapter 12, for a review.

(6) J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Am. Chem. Soc.*, **97**, 1245 (1975), report (footnote 14) that as low as −100 °C $Co_2(CO)_8$ has one sharp line in the ^{13}C spectrum. This coupled with the previous conclusion from ir spectroscopy[7] that the two tautomers $(OC)_3Co(\mu\text{-}CO)_2Co(CO)_3$ and $(OC)_4CoCo(CO)_4$ differ by only 1.3 kcal/mol shows that the potential energy of this system varies by no more than (and probably much less than) 8 kcal/mol over the entire range of configurations between these two extremes.

(7) (a) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); (b) G. Bor, *ibid.*, **19**, 2065 (1963); (c) K. Noack, *Helv. Chim. Acta*, **47**, 1064 (1964).

(8) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 1233 (1974). The extraordinary structure of this molecule as compared to that of $Fe_2(CO)_9$ itself illustrates the extreme sensitivity of structure to replacement of CO groups by other ligands.

(9) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 1351 (1969).

(10) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4155 (1974).

(11) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).

(12) (a) A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and G. W. Jackson, *J. Chem. Soc., Chem. Commun.*, 1042 (1974); (b) L. Milone, S. Aime, E. W. Randall, and E. Rosenberg, *ibid.*, 452 (1975).

(13) This kind of situation has previously been considered for $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$, where a structure with four bridges and D_{2d} symmetry[14] may be (and, we believe, is) thermally accessible, but has not been positively observed spectroscopically, and need not necessarily be postulated to explain the observed CO scrambling.[15,16]

(14) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

(15) F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Am. Chem. Soc.*, **94**, 6191 (1972).

(16) J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J. Chem. Soc., Chem. Commun.*, 807 (1973).

(17) This structure is different from one with three edge bridges and C_{3v} symmetry previously proposed by Wei and Dahl[9] as "the instantaneous structure of the $(Fe_3(CO)_{12})$ molecule in solution." For reasons detailed elsewhere,[3] we do not agree that this proposal satisfactorily explains the ir spectra of solutions and we have proposed a quite different concept (that of fictile character) which, in our opinion, does account for all the experimental data.[3]

(18) The compound crystallizes in space group $P\bar{1}$ with the following unit cell dimensions: $a = 9.272\ (2)$ Å, $b = 13.727\ (2)$ Å, $c = 8.973\ (1)$ Å; $\alpha = 103.44\ (1)°$, $\beta = 120.53\ (1)°$, $\gamma = 90.01\ (1)°$; $Z = 2$; 2304 reflections, Mo radiation, having $2\theta < 45°$ and $I_0 > 3\sigma(I_0)$; $R_1 = 0.061$, $R_2 = 0.091$.

(19) We thank the Robert A. Welch Foundation for support under Grant No. A494.

F. A. Cotton,* J. D. Jamerson

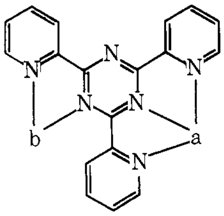
Department of Chemistry, Texas A&M University
College Station, Texas 77843

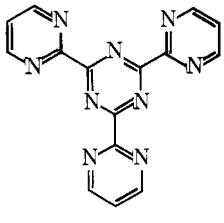
Received March 5, 1976

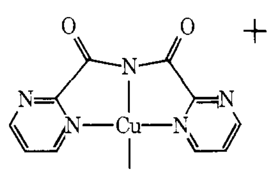
2,4,6-Tris(2-pyrimidyl)- and 2,4,6-Tris(2-pyridyl)-1,3,5-triazines Hydrolyze in the Presence of Copper(II) to Form a Novel Bis(aryl)carboxamidato Chelate Complex

Sir:

The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine, TPyT, has been used analytically in the spectrophotometric determination of iron,[1] ruthenium,[2] and cobalt.[3] Several transition metal and lanthanide complexes of this ligand have been studied,[4-15] the possibility of coordinating metals in both the (a) terpyridine- and (b) bipyridine-like sites being of particular interest.[11-15] The ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine, TPymT, has the potential to coordinate three metal ions in terpyridine-like sites, but has not been extensively studied because of its unavailability.[16,17] In the present report we describe an improved synthesis of TPymT and its reaction with copper(II). Copper promotes hydrolysis of the ligand and forms a novel bis(2-pyrimidyl)carboximidato chelate complex, shown below. This chemistry is also found to occur with TPyT and with other metal ions, knowledge of which is important in conjunction with studies of the coordination properies and with analytical applications of these triazine ligands.







2-Cyanopyrimidine was synthesized by literature methods[18,19] (mp 40-41.5°, lit.[17] 41-42°). This pyrimidine (5.5 g, 0.052 mol) was heated with stirring in a stoppered flask at 150° for 48 h. The solidified product was then pulverized and washed with ether to remove any unreacted starting material. The yield of crude TPymT was 4.6 g (83.6%). Purification was achieved by dissolving 8.0 g of crude product in 150 ml of 6 N HCl, decolorizing with activated charcoal, precipitating the hy-