

increased cage reactivity,³ further synthetic, structural, and theoretical results in this area²³ should lead to a more fundamental understanding of heteroborane chemistry.

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Registry No. H(PMe₃)₂Ir(B₈H₇Cl), 82447-28-7; H(PMe₃)₂(Ph₂PC₆H₄)Ir(B₉H₉), 83251-41-6.

- (23) The preparation and characterization of 10-vertex, 20-skeletal-electron hyper-closo-(mes)Fe(B₉H₉), where mes = η⁶-mesitylene, have recently been reported: Micciche, R. P.; Briguglio, J. J.; Sneddon, L. G. *Inorg. Chem.* **1984**, *23*, 3992.

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Structure and Bonding in Some Recently Isolated Metallaboranes

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Dr. Baker's note¹ emphasizes that there are interesting points regarding the interpretation of the electronic structures of a number of recently reported polyhedral boron-containing cluster compounds. It thereby underlines the need for continued synthetic and further definitive structural work in this area, for the definitive correlation of solid-state and solution structures, for the development of minimum-presumption molecular orbital theories to account for the molecular and proposed electronic structures, and subsequently for the development of definitive experimentation that can be used to assess directly, rather than by inference or intuition, the applicability of any suitable theoretical approaches that may be developed.

A proportion of our work at Leeds is directed at the further exploration of some of these areas, particularly in non-carbon-containing metallaborane clusters, but it is by no means complete. Meanwhile we do not think it unreasonable to entertain the possibility that the metal-to-borane bonding in some of these new structural types may deviate from the assumption, implicit in simple electron-counting rules, that a metal cluster vertex contributes three orbitals with a quasi-conical symmetry to the cluster bonding scheme.²⁻⁵ As a reviewer has emphasized, and we thank him for this, this idea is hardly new or heretical; Wade specifically addressed it 9 years ago in his 1976 electron-counting paper,⁶ and it has been repeatedly invoked since then (see, for example, ref 7).

One of these deviations is that the metal may, in simple terms, contribute four (or more) principal valence orbitals to the cluster bonding, rather than three.^{2-5,8-12} This possibility is not normally

available to boron, since in most known compounds one of the four {s + p³}-type hybrid orbitals is involved in exopolyhedral bonding, although isolated exceptions are recognized, for example in [(CO)₁₂HFe₄BH₂]¹³ (and also, of course, in fused "macropolyhedral" clusters such as B₁₈H₂₂, but in these the formal boron orbital contribution will still remain ≤3 to each of the individual subclusters). A four-orbital interaction may be expected to lead to cluster geometries and electronic configurations not found for simple boranes and carboranes, and it may further be expected that some of these structures would be characterized by higher metal-to-borane connectivities. Both of these features are characteristic of a number of the structures Dr. Baker mentions,¹ and for compounds that we have isolated,^{6,10,14,15} we have sometimes chosen to use the descriptor "isocloso" when these have closed deltahedral structures. It should be emphasized that these particular "isocloso" structures approximate closely to high symmetries (C_{2v} for 9-vertex; C_{3v} for 10-vertex) and are *not* merely distortions either of regular closo symmetries (D_{3h} for 9-vertex; D_{4d} for 10-vertex) or of "capped closo" geometries; one simple generalization mentioned by a second reviewer (whom we also thank) is that the "isocloso" clusters would have the same formal electron count as a closo cluster, but that the metal vertex in the "isocloso" cluster would contribute four orbitals rather than three to the cluster bonding scheme.

It should also be emphasized that an assessment of these four-orbital and related bonding hypotheses, and the assessment of additional related chemistry such as solution equilibration etc.,¹ is often rendered difficult by a number of complicating features. These include the propensity of metals such as ruthenium, rhodium, and iridium to form sixteen- (and sometimes fourteen-) electron metal centers as well as eighteen-electron ones, the ability of clusters in certain circumstances to exist with geometries inappropriate for (more unambiguous) formal Wadlan electron counts (e.g. B₈H₁₂, B₉Cl₉, [(C₅H₅)₄Co₄B₄H₄], [(C₅H₅)₄Ni₄B₄H₄], etc.),¹⁶ and the fact that the effective energetic differences between formal valency states [e.g. iridium(III) vs. iridium(V), or ruthenium(II) vs. ruthenium(IV)] may not be all that great in these types of bonding environment.¹⁷⁻²⁰ These and other factors, of which some are mentioned by Dr. Baker¹ and which include, for example, changes in the π-acidity of the other ligands on the metal atoms,²¹ introduce great flexibility in structural behavior, and simple electron-counting theory is often inappropriate in the absence of other evidence: it is therefore important that each structure is assessed on its merits, rather than by a rigid application of "rules" developed for simpler systems.^{3,19,22}

In this context we find that a blanket use of the descriptor "hypercloso", for closed structures that appear not to conform to perceived "rules", is not universally helpful. Additional difficulties

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arise because at a synthetic level it is still a problem to engineer reaction chemistry to give reasonable yields of isolatable species that may be expected to exhibit features that would be helpful in the assessment of these bonding considerations, whether they be "hypercloso" or "isocloso". At present we would prefer to spend time addressing these synthetic problems.

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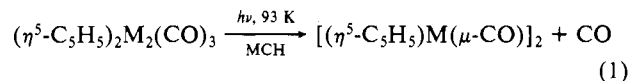
Photochemistry of $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_3$ ($\text{M} = \text{Co}, \text{Rh}$) in Low-Temperature Organic Glasses: Generation of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\mu\text{-CO})]_2$

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We wish to report that near-UV irradiation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_3$ ($\text{M} = \text{Co}, \text{Rh}$) in low-temperature hydrocarbon matrices results in rapid and clean loss of CO to produce the metal-metal-double-bonded, doubly CO-bridged product $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\mu\text{-CO})]_2$. Compounds containing a simple 2e metal-metal bond have been shown to generally yield metal-centered radicals upon photolysis.¹ However, even though metal-centered radicals may dominate the photoproducts in fluid solutions, recent results have shown that photolysis of metal-metal-bonded compounds in rigid matrices may yield products resulting from expulsion of a 2e-donor ligand. Although the photolysis of the compounds $\text{Mn}_2(\text{CO})_{10}$,² $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}_2(\text{CO})_4$,³ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$ ⁴ in fluid solutions results in the formation of radicals arising from net metal-metal bond homolysis, irradiation of these same compounds in rigid matrices gives only the CO loss products $\text{Mn}_2(\text{CO})_9$,⁵ $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_3$,⁶ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_5$,⁷ respectively.

Our interest in the $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_3$ compounds was sparked by reports that irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ in rigid matrices results in formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\mu\text{-CO})]_2$.^{8,9} Prolonged photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ in fluid solution yields small amounts of the thermally unstable $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\mu\text{-CO})]_2$,¹⁰ but the dominant product is $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$.¹¹ Irradiation of ~ 1 mM $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ at 93 K in a rigid methylcyclohexane matrix results in the formation of an alkane oxidative-addition product $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{H})(\text{C}_7\text{H}_{13})$, although at higher concentrations (>5 mM) an additional product, $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})]_2$, is formed.⁹ At room temperature the irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ in alkane solution results in formation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$.¹² The crystal structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$ reveals that the molecule contains a metal-metal bond and is singly bridged and that the $(\eta^5\text{-C}_5\text{H}_5)$ groups are trans to each other.¹² We were interested in determining whether the $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\mu\text{-CO})]_2$ complexes observed in the matrix studies could be the products of photolysis of the metal-metal-single-bonded dimers $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_3$. Though no quantitative data were provided, it has been previously noted that irradiation at room temperature of the related complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\text{CO})_3$ results in formation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$.¹³ Irradiation of $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})_2$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$ at room temperature results in $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\mu\text{-CO})]_2$ and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$,^{14,15} respectively. We now report that photoreaction according to eq 1 occurs rapidly and cleanly at low temperature,



establishing CO loss as the only efficient photoreaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_3$ in a low-temperature rigid matrix.

Experimental Section

Instruments. IR spectra were recorded by using either a Nicolet 7199 or 60SX Fourier transform interferometer. UV-vis spectra were obtained with the use of either a Cary 17 spectrophotometer or a Hewlett-Packard 8451A diode array spectrophotometer. Low-temperature IR and UV-vis spectra were obtained by using a Specac Model P/N 21000 variable-temperature cell with CaF_2 outer windows using liquid N_2 as the coolant. A small hole drilled into the metal portion of the sample cell accommodates the junction end of a copper-constantan thermocouple. Irradiations were carried out with use of either a 450-W medium-pressure Hanovia Hg lamp with a quartz, H_2O -cooled jacket or a Bausch and Lomb SP 250-W high-pressure Hg lamp. The Bausch and Lomb lamp was used with a 10-cm H_2O filter with Pyrex windows to filter out IR and deep-UV irradiation.

Chemicals. Hexane was distilled from CaH_2 under N_2 before use. Methylcyclohexane (MCH) was distilled from Na under Ar before use. CH_2Cl_2 was chromatographic grade and deoxygenated before use. Generally, all manipulations of organometallic compounds were carried out under N_2 or Ar by using a Vacuum Atmospheres drybox or conventional Schlenk-line techniques. The known¹¹ $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ was prepared by irradiation (General Electric Blacklight bulbs) of a dilute (~ 0.03 M) hexane solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$. The solvent was stripped and the residue chromatographed on alumina. $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ was eluted with hexane, after which $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ was eluted with CH_2Cl_2 . The solvent was then removed by vacuum. A similar procedure was used for the preparation of the known¹² $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$. $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$ was prepared according to the literature method.¹⁷

Results and Discussion

Figure 1 shows IR spectral changes resulting from near-UV irradiation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$ in methylcyclohexane glasses at 93 K. The terminal (1965 cm^{-1}) and bridging (1812 cm^{-1}) CO bands of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ can be seen to decrease upon irradiation. Free CO (2132 cm^{-1})¹⁸ is produced upon consumption of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$, as well as a material with a strong CO absorption in the bridging region at 1792 cm^{-1} , which is assigned to the doubly bridged dimer

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