Conditions for the Occurrence of Bridging Carbonyl Groups

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Sir:

In the course of recent investigations of the structural, dynamical, and bonding properties (all of which are, of course, interrelated closely) of polynuclear metal carbonyls, we have been led to believe that the following generalization is valid: "*Bridging carbonyl groups never occur unless the bridged metal atoms are formally bonded to each other.*"

The empirical validity of this statement clearly depends on there being no known exceptions. To our knowledge, only one apparent exception has been mentioned in the literature. We report here our reinvestigation of this *apparent* exception, *viz.*, $[(\eta^5\text{-}C_5H_5)Rh(CO)_2]_2$,[1] and show that the compound does not exist.

It was reported that exposure of a petroleum ether (bp 50-70°) solution of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ to air for 3 weeks produces a red, crystalline substance, **1**, to which the formula $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_4$ was assigned. The infrared spectrum indicated that both bridging and terminal CO ligands are present. The compound was reported to melt with decomposition (turning black) at 123°. Subsequently, Mills and Nice[2] undertook to determine the crystal structure of the compound. However, in order to speed up the preparative process, they irradiated the solution of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$. They obtained a red crystalline material which they initially assumed to be **1**, but the X-ray crystallographic analysis showed it to be $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$, **2**. The infrared and nmr spectra of **2** have since been reported.[3] The compound has a Rh-Rh bond and one bridging CO ligand. The suspicion that **1** was incorrectly formulated and is identical with **2** comes readily to mind. However, to minimize uncertainty it was considered mandatory to reinvestigate **1**, preparing it exactly as directed by Fischer and Bittler.

In a small Schlenk tube, dry air was passed slowly over a solution of 20 mg of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in 1.5 ml of petroleum ether for 10 days. Some red crystals and some black crystals were formed in the tube. One of these red crystals was placed in an evacuated, sealed capillary and heated. It decomposed, turning black, over the temperature range 119-125°. This is in reasonable agreement with the decomposition temperature of 123° reported[1] for **1**.

The ir spectrum of the red substance we prepared by Fischer and Bittler's method has broad bands at 1950 ± 10 and 1800 ± 10 cm^{-1} when measured in a KBr pellet, and sharp bands at 1985 ± 3 and 1839 ± 3 cm^{-1} when measured on a hexane solution. The former values agree reasonably well with those (1961, 1812 cm^{-1}) given by Fischer and Bittler for **1**, although it is impossible to make a completely definite comparison since these authors did not state the medium in which the spectrum was measured. The values we find in hexane agree to within experimental error with the values reported[3] for **2** in the same solvent.

Another red crystal was mounted for X-ray examination and the unit cell dimensions were measured. The results were as follows, where the dimensions of **2** as reported by Mills and Nice are given in brackets: $a = 8.06\ (3)$ Å [8.08 (4) Å], $b = 9.04\ (2)$ Å [8.95 (5) Å], $c = 9.45\ (3)$ Å [9.46 (5) Å], $\alpha = 73.8\ (2)°$ [73° 8′ (10′)], $\beta = 80.7\ (2)°$ [80° 30′ (10′)], $\gamma = 83.3\ (2)°$ [83° 9′ (10′)], $V = 651\ (3)$ Å^3 [644 Å^3].

We conclude on the basis of all of the foregoing data that compound **1**, $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_4$, which would be expected to have two bridging CO groups but no Rh-Rh bond does not in fact exist and that the substance reported to be **1** is really **2**.

The occurrence of bridging CO groups only across pairs of metal atoms which are formally bonded to each other could be attributed simply to the fact that nonbonded metal atoms would necessarily be too far apart to allow the formation of the M-C bonds without at the same time requiring the M-C-M angle to be excessively large. However, we believe that the reason is more complex. Braterman[4] has recently suggested that the representation of a CO bridge moiety as a kind of inorganic ketone, with two localized electron-pair bonds from each of the metal atoms to the carbon atom, is a considerable, and misleading, oversimplification. He has further indicated qualitatively what additional complexities might exist in the four-center M_2CO moiety.

These include a "nonseparability" of the M-C and M-M bonds, arising from the importance of three-center overlaps between orbitals which are suitable for M-M bonding and the carbon 2s and 2p orbitals.

We would welcome information on any other apparent exceptions (if there are any) to the generalization proposed above.

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