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Preliminary communication

MONOMETALLIC AND BRIDGED BIMETALLIC (INCLUDING MIXED METAL) COMPLEXES OF 2,3-DIAZABICYCLOHEPT-2-ENE WITH GROUP VIB TETRACARBONYL MOIETIES

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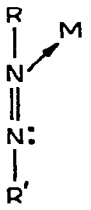
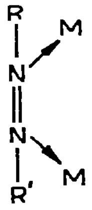
Summary

Complexes of the type $M(CO)_4L_2$ (L = 2,3-diazabicyclohept-2-ene; M = Cr, Mo, W) and the bridging systems $(CO)_4ML_2M'(CO)_4$ (M = M' = Mo; M = Mo, M' = Cr) have been prepared.

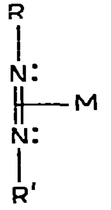
There has been considerable recent interest in the chemistry of compounds which contain an azo linkage ($-\ddot{N}=\ddot{N}-$) coordinated to a transition metal center [1,2]. This interest arises in part from the proposal that a transition metal complex of diazene (HN=NH) may be an intermediate in the enzymatic fixation of dinitrogen [3]. Examples of the structural types I-IV are now known [1,2] in which the azo linkage is coordinated through one or both nitrogen lone pairs (I, II), through the N=N π bond (III), or through both the lone pairs and the π bond simultaneously (IV). Sellmann has even reported transition metal organometallic complexes of diazene of types I and II [4]. We now report the synthesis of two significant new types of complexes of structural types I and II.



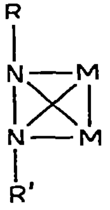
(I)



(II)

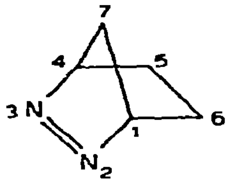


(III)

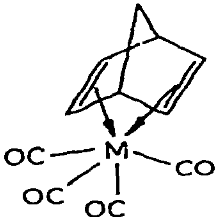


(IV)

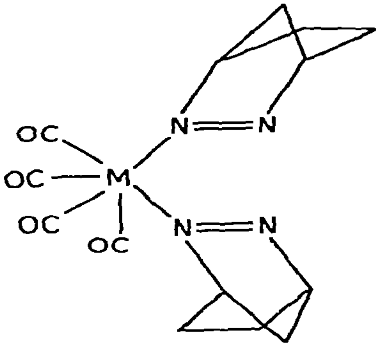
Stirring equimolar amounts of 2,3-diazabicyclohept-2-ene (V, $C_5H_8N_2$), and bicyclo[2.2.1]heptadienechromium tetracarbonyl (VI, M = Cr), in hexane at room temperature under nitrogen for several hours produces an orange-red precipitate in near quantitative yield formulated as $(CO)_4Cr(C_5H_8N_2)_2$ on the basis of analysis and molecular weight (found 316, calcd. 356)*. The infrared spectrum in dichloromethane shows a typical tetracarbonyl pattern for a *cis* disubstituted octahedral complex with bands at 2020 m, 1942 w (sh), 1910 s, and 1850 m cm^{-1}. The NMR spectrum shows two overlapping singlets at τ 4.83 and 4.92 and a multiplet at τ 8.0-9.2 with relative areas 1/1/6**. The two singlets reveal that the two bridgehead hydrogen atoms 1 and 4 of the azo ligand V are inequivalent and that type I coordination occurs. A similar NMR pattern has been observed in other type I complexes of V [5]. These data support structure VII (M = Cr) for the complex. The same reaction using VI (M = W) as reactant yields orange-red $(CO)_4W(C_5H_8N_2)_2$ (VII, M = W) with carbonyl bands at 2020 m, 1900 s, and 1845 m cm^{-1} and two distinct singlets in the NMR at τ 4.78 and 4.91 for the bridgehead protons. While numerous azo complexes of type I are known the compounds VI with M = Cr or W are the first examples in which more than one azo linkage is coordinated to a single metal atom in a monometallic complex.



(V)



(VI)



(VII)

Under the same reaction conditions V and VI (M = Mo) deposit a solid which is a mixture of $(CO)_4Mo(C_5H_8N_2)_2$ (VII, M = Mo) and another complex $Mo_2(CO)_8(C_5H_8N_2)_2$ (VIII, M = M' = Mo). Separation methods promote the conversion of $(CO)_4Mo(C_5H_8N_2)_2$ to $Mo_2(CO)_8(C_5H_8N_2)_2$ and it has not yet been possible to isolate pure $(CO)_4Mo(C_5H_8N_2)_2$. However, pure $Mo_2(CO)_8$-$(C_5H_8N_2)_2$ can be obtained by chromatography of the mixture on Florisil. The air-stable red-brown solid (mol.wt.: found 615, calcd. 608) shows five carbonyl bands at 2043 m, 2010 s, 1948 s, 1920 vs, and 1882 s cm^{-1} in dichloromethane. The NMR spectrum gives a singlet at τ 4.90 and multiplet at τ 7.9-9.2 with relative areas of 1/3. The unsplit τ 4.90 resonance indicates that protons 1 and 4 in the ligand are equivalent in the complex and supports a bridging structure VIII (M = M' = Mo) such as that found for the tris-bridged complex $Cr_2(CO)_6(C_5H_8N_2)_3$ [5]. The five carbonyl frequencies observed are less than the seven predicted for a maximum C_{2v} symmetry, but more than the four bands expected if the two tetracarbonyl units are identical and inde-

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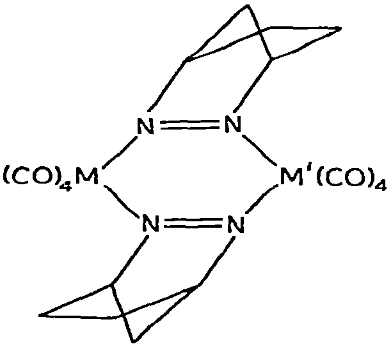
* All new compounds reported gave satisfactory analyses for the elements C, H, and N.

** NMR spectra taken in $CDCl_3$ with internal tetramethylsilane as reference on a Varian A60 instrument.

pendent. Compounds of type II containing one [1,2,4] and three [5] bridging azo linkages have been reported. $Mo_2(CO)_8(C_5H_8N_2)_2$ with two bridging azo linkages fills the previous gap in this series.



(VIII)

During its synthesis $(CO)_4Cr(C_5H_8N_2)_2$ (VII, M = Cr) did not react with excess $(C_7H_8)Cr(CO)_4$ (VI, M = Cr) to give a bridging complex. However, a suspension of $(CO)_4Cr(C_5H_8N_2)_2$ in hexane at room temperature does react with $(C_7H_8)Mo(CO)_4$ (VI, M = Mo) to give, after chromatography on Florisil, black crystals of formula $CrMo(CO)_8(C_5H_8N_2)_2$. The infrared spectrum of this compound in dichloromethane shows carbonyl bands at 2035 m, 2005 s, 1940 s, 1912 vs, and 1872 s cm^{-1}; this pattern resembles that of the bridging molybdenum complex VIII (M = M' = Mo). The NMR spectrum shows only a single peak at τ 4.87 for the bridgehead protons of the ligand indicating that they are in identical or nearly identical environments. Thus $CrMo(CO)_8(C_5H_8N_2)_2$ appears to have structure VIII (M = Mo, M' = Cr) in which two bridging azo ligands join two different metal atoms. This compound represents the first example of an azo ligand functioning in this manner. Compounds of this structure are of particular interest because of the possibility that diazene may be coordinated simultaneously to both iron and molybdenum in the enzymatic fixation of dinitrogen [3]. Further work with VII (M = Cr or W) and similar compounds is expected to lead to an extensive series of the heretofore unavailable azo-bridged mixed metal compounds of type VIII.

Acknowledgements

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