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Preliminary communication

NOVEL BINUCLEAR RHODIUM COMPLEXES CONTAINING KETONIC CARBONYL AND ACETYLENE LIGANDS

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Summary

The reactions of *trans*-$[RhCl(CO)(DPM)]_2$ ($DPM = Ph_2PCH_2PPh_2$) with dimethylacetylenedicarboxylate (DMA) and hexafluoro-2-butyne (HFB) yield the novel species $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}Acet)(DPM)_2]$ (Acet = DMA, HFB). The X-ray structure determination of the DMA derivative indicates that the complex has the acetylene molecule coordinated as a *cis*-dimetallated olefin and also contains a ketonic carbonyl ligand. The long Rh···Rh separation (3.3542(9) Å) suggests no metal—metal bond and the Rh—C(O)—Rh angle (116.0 (4)°) suggests sp^2 hybridization of the carbonyl carbon atom. Similarly the geometry at the acetylene ligand and the C—C distance of the coordinated acetylene moiety (1.32(1) Å) are consistent with the dimetallated olefinic formulation. This represents the first reported characterization of a ketonic carbonyl complex outside the Ni triad. These novel complexes have also been formed by the direct insertion of the acetylene molecules into the formal Rh—Rh bond in $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$.

The preparation and characterization of polynuclear complexes and their chemistry with small molecules are presently of considerable interest, particularly when the small molecules display unusual coordination modes [1—4]. One such unusual coordination mode involves the ketonic carbonyl ligand* which, to date, has been structurally characterized for only two very similar complexes of Pd [1] and Pt [2]. No such complex of rhodium has yet been characterized, although we have postulated the existence of such species as intermediates in reactions involving *trans*-$[RhCl(CO)(DPM)]_2$ ($DPM = Ph_2PCH_2PPh_2$) with small molecules [5, 6]. Further characterizations of ketonic carbonyl complexes, particularly outside of the Ni triad, would be of tremendous value in leading to an understanding of the factors which stabilize this unusual bonding mode.

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*The term, "ketonic" carbonyl refers to a carbonyl ligand which bridges two metals not bonded to each other.

The coordination modes of acetylene molecules in polynuclear complexes are also of current interest [3, 4, 7—11]. For an acetylene molecule bridging two metal atoms two coordination modes can be considered; the more common, being a μ_2-η^2 interaction, having a tetrahedral M_2C_2 framework [7, 12, 13] and the second, less common mode being viewed as a *cis*-dimetallated olefin complex, for which few examples have been structurally characterized [3, 4, 9]. It is of interest to obtain structural information on the coordination of acetylenes in binuclear complexes in order to correlate the effect of structure on the subsequent chemistry of these species.

We report here our preliminary results on the reactions of *trans*-[RhCl(CO)(DPM)]$_2$ (I) with activated acetylenes, yielding novel complexes containing both a ketonic carbonyl ligand and an acetylene molecule coordinated as a *cis*-dimetallated olefin. These are the first rhodium complexes to be characterized containing this unusual carbonyl coordination mode and the first complexes where both a ketonic carbonyl ligand and an acetylene molecule, bonded as a *cis*-dimetallated olefin, are present in the same complex.

The treatment of I (200 mg in 10 ml CH_2Cl_2) with 50 mg of dimethylacetylenedicarboxylate (DMA) under a dinitrogen atmosphere and precipitation after 15 mins with diethyl ether yields a green solid (II) having a broad carbonyl stretching vibration at ca. 1700 cm^{-1} and a $^{31}P\{^1H\}$ NMR spectrum (δ 9.9 ppm, $|^1J(Rh—P) + {}^xJ(Rh—P)| = 141.6$ Hz)* characteristic of a symmetric species. Exposure of a methylene chloride solution of I to one atmosphere of hexafluoro-2-butyne (HFB) results in the precipitation, after several hours, of a green highly insoluble solid (III) having a medium intensity band in its infrared spectrum at 1705 cm^{-1} and a symmetrical $^{31}P\{^1H\}$ NMR spectrum similar to that of the DMA species (δ 8.9 ppm, $|^1J(Rh—P) + {}^xJ(Rh—P)| = 131.8$ Hz). No evidence of a perturbed acetylene stretching vibration is observed for either complex. The low value for ν(CO) in the HFB complex suggests a ketonic carbonyl species**; the analogous vibration in the DMA complex is masked by the carboxylate vibrations near 1700 cm^{-1}. The presence of the bridging carbonyl ligand in the DMA complex is confirmed by the infrared and $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra of a ^{13}CO enriched sample which have $\nu(^{13}CO)$ 1660 cm^{-1} and an unresolved ^{13}C resonance at δ 181 ppm***, respectively. Elemental analyses for both II (C, H, Cl, O) and III (C, H, Cl) are consistent with the formulation [Rh_2Cl_2(μ-CO)(μ-acetylene)(DPM)$_2$]. The structure of the DMA derivative was undertaken, owing to a lack of suitable crystals of the HFB analogue, in order to verify the ketonic carbonyl formulation and to establish the acetylene bonding mode.

[Rh_2Cl_2(μ-CO)(μ-DMA)(DPM)$_2$] (II), crystallizes in the space group $P4_12_12$ with a 15.021(2) Å, c 25.738(6) Å, V 5807 Å^3 and $Z = 4$. Intensity data were collected on an automated Picker four circle diffractometer using nickel filtered Cu-K_α radiation in the range $3° \leqslant 2\theta \leqslant 124°$. Of the 5023 unique reflections measured 4566 were observed ($I \geqslant 3\sigma(I)$) and were used in the solution and

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*All positive shifts downfield from external H_3PO_4.

**The value of ν(CO) is obviously in the range of organic carbonyls since it is masked by the carboxylate vibrations in complex II. However, it is recognized that CO stretches in DPM-bridged complexes are not strongly correlated to structure. See ref. 2 and 14 for example.

***Complex [Rh_2Cl_2(μ-CO)(μ-DMA)(DPM)$_2$] is not very soluble so well resolved $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra were not obtained. The analogous bromo and iodo complexes, however, show the expected well resolved triplets at δ 184.5 and 191.8 ppm, respectively.

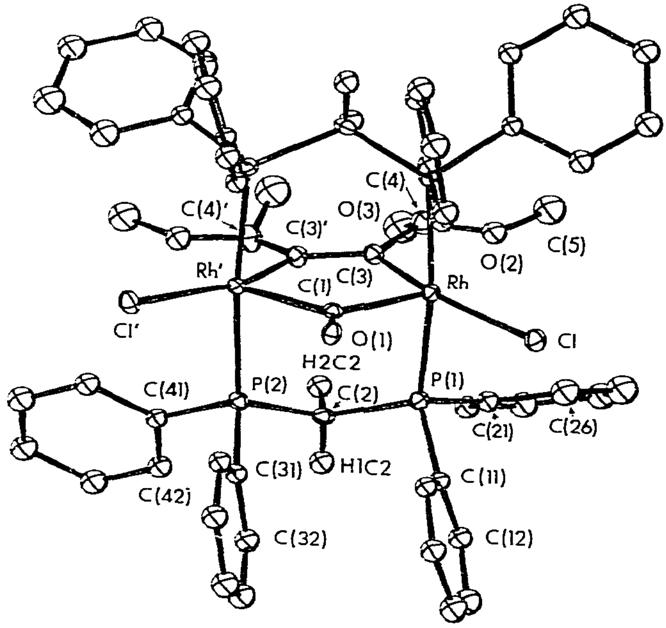

Fig. 1. A perspective view of [Rh$_2$Cl$_2$(μ-CO)(μ-DMA)(DPM)$_2$] showing all non hydrogen atoms with 20% thermal ellipsoids. Only one set of disordered positions for O(2), O(3) and C(5) is shown. Methylene hydrogen atoms are drawn artificially small.

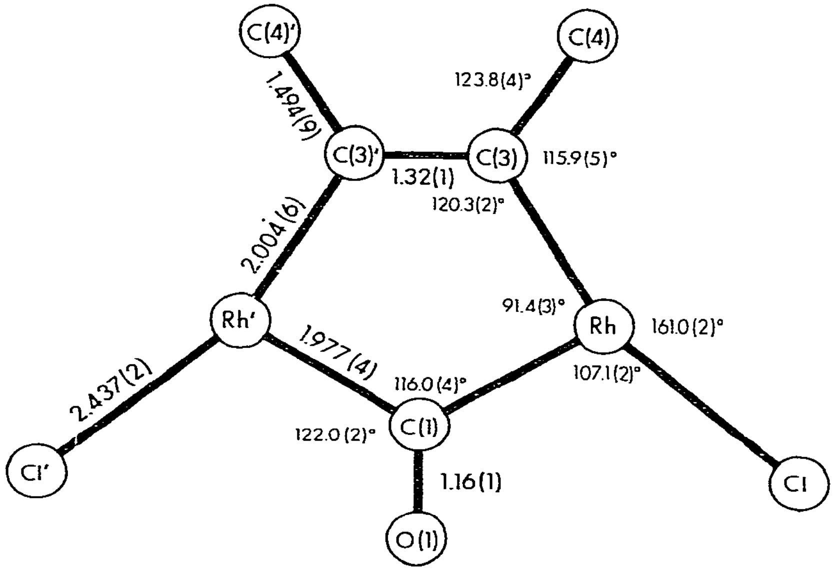

Fig. 2. A representation of the coordination in the approximate plane of the acetylene and carbonyl ligands showing some relevant bond lengths and angles. Rh···Rh 3.3542(9) Å.

refinement of the structure, which was solved by conventional Patterson and Fourier methods and refined by full matrix least-squares techniques to R = 0.049 and R_w = 0.066. At the present stage of refinement the carboxylate groups (O(2), O(3) and C(5), see Fig. 1) are disordered between two positions. The disordered atoms were refined isotropically with 50% occupancy of each position. All other non-hydrogen atoms were refined anisotropically. The phenyl rings are refined as rigid groups with C—C 1.392 Å, fixed hydrogen contributions are included and the data are corrected for absorption effects.

The molecule, shown in Fig. 1, sits across the crystallographic two fold axis which is colinear with the bridging carbonyl group (C(1)O(1)) and bisects the Rh···Rh axis and the acetylene molecule. Only one set of disordered positions for O(2), O(3) and C(5) is shown. This structure determination confirms the unusual ketonic carbonyl bonding mode and establishes the *cis*-dimetallated olefin formulation for the acetylene molecule. Figure 2 shows a representation of the coordination in the plane of the acetylene and carbonyl ligands along with the relevant parameters. All structural parameters involving the bridging carbonyl ligand are consistent with its formulation as a ketonic carbonyl species. Therefore, the long Rh···Rh separation (3.3542(9) Å) indicates no formal Rh—Rh bond and the angles about C(1) indicate sp^2 hybridization of this atom. Similarly the parameters about the acetylene ligand agree with its formulation as a *cis*-dimetallated olefin. The C(3)—C(3)′ bond, at 1.32(1) Å, is consistent with a C=C double bond and the angles about C(3) are close to the expected value of 120° and agree well with the related palladium complex [3]. The olefinic moiety is twisted slightly about the C(3)—C(3)′ bond with an average torsion angle (e.g. Rh—C(3)—C(3)′—C(4)′) of ca. 10°.

The structural characterization of this acetylene species suggested that these complexes could also be prepared by the direct insertion of the acetylene molecules into the formal Rh—Rh bond of [$Rh_2Cl_2(\mu\text{-CO})(DPM)_2$] [14]. This has been verified for both the HFB and DMA molecules, the reactions taking place immediately in CH_2Cl_2 solution yielding green solids having the expected spectral properties and elemental analyses. Attempts to remove the ketonic carbonyl ligand from complex III with trimethylamine oxide at room temperature in CH_2Cl_2 did not succeed. However, on refluxing complex III in $CHCl_3$ with a 10-fold excess of trimethylamine oxide the carbonyl group is slowly removed over a period of 24 h yielding the carbonyl-free complex, [Rh_2Cl_2-(μ-HFB)$(DPM)_2$] (IV) which shows a perturbed acetylene stretch at 1638 cm^{-1} and has a $^{31}P\{^1H\}$ NMR spectrum characteristic of a symmetrical species (δ 7.5 ppm, $|^1J(Rh—P) + {}^xJ(Rh—P)|$ = 111.8 Hz) [15]. Species IV has been prepared by another route and has been shown to react readily with CO [15] yielding complex III. A crystallographic study of complex IV is underway in order to establish the acetylene bonding mode. The difficulty in removing the carbonyl ligand from complex III is in contrast to the facile CO removal from the related DPM palladium [16] and platinum [17] ketonic carbonyl species and resembles more the sluggish CO loss reported for the DAM* palladium and platinum analogues [16, 17].

The characterization of these unusual species represents a significant contri-

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*Abbreviations used: Cp = η^5-C_5H_5, DAM = $Ph_2AsCH_2AsPh_2$.

bution to the understanding of the factors which stabilize ketonic carbonyl ligands, with [$Rh_2Cl_2(\mu$-CO)(μ-DMA)(DPM)$_2$] being the first structurally characterized ketonic carbonyl complex outside the Ni triad. The Rh···Rh separation observed is by far the largest distance yet to be bridged by a carbonyl ligand. This observation is even more significant when one considers that the ketonic carbonyl and associated *cis*-dimetallated olefin coordination of the acetylene molecule in the present complex are favoured over the alternate structure which would have a stable closed shell configuration, a "normal" bridging carbonyl ligand, a formal metal—metal bond and a μ_2-η^2 acetylene coordination, as was observed for [$Cp_2Rh_2(\mu$-CO)(μ-HFB)] [13].

Based on these results and those of the related Pd [1] and Pt [2] species it is clear that previous ideas on the bonding in bridging carbonyl complexes must be reconsidered. When the only bridging group is a carbonyl ligand, previous arguments [18, 19] that a formal metal—metal bond is required still seems valid. However in the presence of bridging groups such as DPM and DAM it is now evident that a formal metal—metal bond is not a prerequisite to a stable bridging carbonyl complex.

Tables of atomic positions, thermal parameters and selected bond lengths and angles and observed and calculated structure factors are available*.

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References

1 (a) R. Colton, M.J. McCormick and C.D. Pannan, J. Chem. Soc., Chem. Commun., (1977) 823; (b) R. Colton, M.J. McCormick and C.D. Pannan, Aust. J. Chem., 31 (1978) 1425.
2 M.P. Brown, A.N. Keith, Lj. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt and K.R. Seddon, Inorg. Chim. Acta, 34 (1979) L223.
3 A.L. Balch, C. Lee, C.H. Lindsay and M.M. Olmstead, J. Organometal. Chem., 177 (1979) C22.
4 R.S. Dickson, S.H. Johnson and H.P. Kirsch, Acta. Crystallogr. B, 33 (1977) 2057.
5 M. Cowie and S.K. Dwight, Inorg. Chem., 19 (1980) 209.
6 M. Cowie and S.K. Dwight, Inorg. Chem., in press.
7 E.L. Muetterties, W.R. Pretzer, M.G. Thomas, B.F. Beier, D.L. Thorn, V.W. Day and A.B. Anderson, J. Amer. Chem. Soc., 100 (1978) 2090 and ref. therein.
8 K. Yasufuku and H. Yamazaki, J. Organometal. Chem., 35 (1972) 367.
9 J.L. Davidson, W. Harrison, D.W.A. Sharp and G.A. Sim, J. Organometal. Chem., 46 (1972) C47.
10 R. Mathieu and R.J. Poilblanc, J. Organometal. Chem., 142 (1977) 351.
11 R.S. Dickson and G.N. Pain, J. Chem. Soc., Chem. Commun., (1979) 277.
12 N.M. Boag, M. Green, J.A.K. Howard, J.L. Spencer, R.F.D. Stansfield, F.G.A. Stone, M.D.O. Thomas, J. Vincente and P. Woodward, J. Chem. Soc., Chem. Commun., (1977) 930.
13 R.S. Dickson, G.N. Pain and M.F. MacKay, Acta Crystallogr. B, 35 (1979) 2321.
14 M. Cowie and S.K. Dwight, Inorg. Chem., in press.
15 M. Cowie and R.S. Dickson, unpublished results.
16 L.S. Benner and A.L. Balch, J. Amer. Chem. Soc., 100 (1978) 6099.
17 M.P. Brown, R.J. Puddephatt, M. Rashidi and K.R. Seddon, J. Chem. Soc. Dalton, (1978) 1540.
18 F.A. Cotton and D.L. Hunter, Inorg. Chem. 13 (1974) 2044.
19 P.S. Braterman, Struct. Bonding (Ber.), 10 (1972) 57.

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