Preparation and Structure of an Unusually Stable Cationic μ-Carbyne Complex of Rhodium

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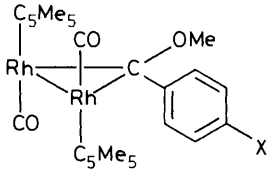
The reaction of either $[(\eta^5\text{-}C_5Me_5)_2Rh_2(CO)_2\{\mu\text{-}C(OMe)Ar\}]$ or $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}C(OMe)Ar\}]$ with $H[BF_4]\cdot OEt_2$ yields the stable cationic carbyne complex $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CAr)][BF_4]$; the structure of the complex for which Ar = $4\text{-}MeC_6H_4$, with a $[BPh_4]$ counterion, was established in an *X*-ray diffraction study.

In recent years there has been considerable interest in the preparation of organometallic complexes in which carbene or carbyne ligands bridge two metal centres. The novel preparation of the bridging methoxycarbene complexes, (**1a**) and (**1b**), from $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2]$ and the arylmethoxy diazirine complexes has been described.[1] Thermolysis of (**1a**) and (**1b**) respectively gave, irreversibly, the bridging monocarbonyls, (**2a**) or (**2b**), as air sensitive blue–black crystals. We now report the reactions of these complexes with acid (or $[Me_3O][BF_4]$), to give the related μ-carbyne complexes, which proved to be unusually stable.

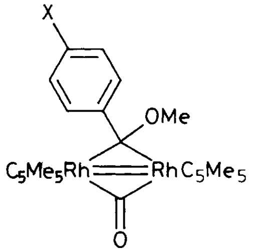
Treatment of an ether solution of the bridging carbene complex, $[(\eta^5\text{-}C_5Me_5)_2Rh_2(CO)_2\{\mu\text{-}C(C_6H_4\text{-}4\text{-}Me)OMe\}]$, (**1a**) with an excess of $H[BF_4]\cdot OEt_2$ resulted in the precipitation of a dark purple solid in essentially quantitative yield. This was isolated by filtration and recrystallised from CH_2Cl_2/Et_2O to give purple–black fibrous crystals, $[(\mathbf{3})][BF_4]$ m.p. 235—236 °C (decomp.), with a greenish metallic lustre. The new complex dissolved readily in Me_2CO, CH_2Cl_2, or EtOH giving intensely coloured magenta solutions, which were stable to air and moisture. The protonation of (**2a**) in CD_2Cl_2 solution was also investigated; the colour of the solution changed rapidly from blue, through red, to magenta, and the identical cation, (**3**), was formed. This strongly suggested that the product contained a single bridging carbonyl group, and that protonation of (**1a**) was accompanied by decarbonylation.

The ^1H n.m.r. spectrum of the complex clearly revealed the lack of the methoxy group, this being confirmed by the ^{13}C n.m.r. spectrum. In addition, in the ^{13}C n.m.r. spectrum, resonances were observed at δ 234.9 (triplet J_{RhC} 54 Hz) and δ 380.5 (triplet, J_{RhC} 51 Hz) which were assigned respectively to the bridging carbonyl and bridging carbyne carbon atoms. The bridging nature of the carbonyl group was confirmed by i.r. spectroscopic data, (ν_{CO} = 1855 cm^{-1}, CH_2Cl_2). The marked shift to higher wavenumber in comparison with (**2a**) (ν_{CO} = 1762 cm^{-1}) reflects a sharp decrease in back-donation to the ligand, as would be expected for a cationic species.

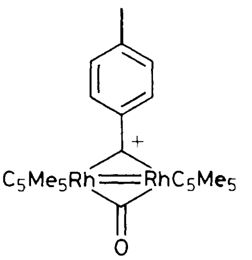
It did not prove possible to grow crystals of the tetrafluoro-



(1) a; X = Me
b; X = F



(2) a; X = Me
b; X = F



(3)

borate salt of (**3**) suitable for an *X*-ray diffraction study, but suitable crystals were obtained of the tetraphenylborate salt.[†] There were two crystallographically distinct molecules in the unit cell. The structure (Figure 1) confirms that this is a bridged monocarbonyl complex, with the two rhodium atoms, the carbyne, and the carbonyl carbon atoms forming a planar Rh_2C_2 four-membered ring. The rhodium–rhodium distance (2.56 and 2.57 Å in the crystallographically distinct molecules) is closely comparable to the only other value reported in the literature {2.56 Å for $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2]$}.[2] There is no interaction between the aryl ring and either of the metal centres. An interesting feature of the structure is that in one of the crystallographically distinct molecules the pentamethylcyclopentadienyl rings are eclipsed, whilst in the other they are staggered. In both cases the methyl groups are bent away from the metal centre, and the plane of the aryl ring lies virtually parallel to those of the pentamethylcyclopentadienyl ligands, presumably to alleviate steric crowding.

The unusual stability of this complex in comparison with other unsaturated dirhodium complexes could be due to two factors. Firstly, the cationic carbyne centre is sterically protected from attack by the bulk of the Cp* (Cp* = C_5Me_5) ligands. It could also be postulated that the positive charge on the carbon atom may be delocalised around the dimetallacyclopropene ring in a 2π aromatic system. The fact that both (**1a**) and (**2a**) reacted with $H[BF_4]$ to give the same product, (**3**), is worthy of comment. It might be suggested that a dicarbonyl carbyne complex would be inherently unstable, losing CO spontaneously, but this seems unlikely in view of the reasonable stability of the analogous $[Cp_2Co_2(CO)_2(\mu\text{-}CMe)][BF_4]$ (Cp = C_5H_5).[4] One explanation might be that (**1a**) is in equilibrium with (**2a**), with protonation of (**2a**) strongly favoured over that of (**1a**).

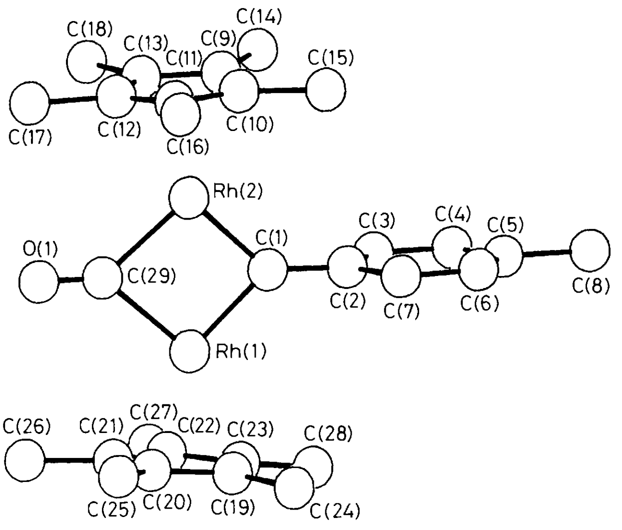


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4\text{-}4\text{-}Me)]^+$, (**3**): dimensions Rh(1)–Rh(2) 2.571(1), Rh(1)–C(1) 1.922(12), Rh(1)–C(29) 1.967(12), Rh(1)–Cp(2) 1.858, Rh(2)–C(1) 1.896(10), Rh(2)–C(29) 1.960(14), Rh(2)–Cp(1) 1.845, O(1)–C(29) 1.17(2) Å; Rh(2)–Rh(1)–C(1) 47.2(3), Rh(2)–Rh(1)–C(29) 49.0(4), Rh(2)–Rh(1)–Cp(2) 174.0, C(1)–Rh(1)–C(29) 96.2(5), C(1)–Rh(2)–C(29) 97.3(5), C(1)–Rh(1)–Cp(2) 138.4, C(29)–Rh(1)–Cp(2) 125.4, Rh(1)–Rh(2)–C(1) 48.1(3), Rh(1)–Rh(2)–C(29) 49.2(3), Rh(1)–Rh(2)–Cp(1) 173.7, C(1)–Rh(2)–C(29) 97.3(5), C(1)–Rh(2)–Cp(1) 137.9, C(29)–Rh(2)–Cp(1) 124.8, Rh(1)–C(1)–Rh(2) 84.7(5), Rh(1)–C(1)–C(2) 136.5(7). Structural data for only one of the crystallographically distinct molecules in the unit cell are presented; bond lengths and angles are not significantly different in the other unit. Cp(1) and Cp(2) refer to the centroids of the pentamethylcyclopentadienyl rings.

The protonation of methoxy substituted μ-carbene complexes has proved a useful route to a range of carbyne complexes. Previous applications have involved μ-carbene complexes prepared by reaction of Fischer type carbene complexes such as $[PhC(OMe){=}Cr(CO)_5]$ with co-ordinatively unsaturated metal species such as $[Pt(PR_3)_2(C_2H_4)]$.[5] The present diazirine-based synthesis represents an entirely new route, applicable to a wide range of systems. Since (**3**) may be converted to (**2a**) by addition of methoxide ion, this work may also provide an entry to a range of other substituted μ-carbene complexes.

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[†] *Crystal data*: $[(\mathbf{3})][BPh_4]$, $C_{53}H_{57}BORh_2$, M = 926.7, triclinic, space group $P\bar{1}$, a = 10.996(8), b = 15.606(6), c = 27.692(4) Å, α = 101.91(2), β = 101.86(4), γ = 91.08(4)°, U = 4541.3 Å^3, Z = 4, D_c = 1.36 g cm^{-3}, monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 7.5 cm^{-1}. Data were collected on an Enraf–Nonius CAD4 diffractometer. A total of 11802 unique reflections were measured in the range $2 < \theta < 22°$ and $+h \pm k \pm l$, and 8172 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement. There was no crystal decay and no absorption correction was made. The structure was solved by routine heavy atom methods and refined by full matrix least squares with the rhodium atoms anisotropic. Hydrogen atoms were omitted, the weighting scheme was $\omega = 1/\sigma^2(F)$ and the final residuals were R = 0.077, R' = 0.101. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.