

Synthesis of the First Example of a Cyclometallated *ortho*-Nitrophenyl Complex. X-Ray Molecular Structure of Carbonyl(chloro)bis(*o*-nitrophenyl-*C,O*)rhodium

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The complex $[\text{RhCl}(\text{CO})_2]_2$ reacts at room temperature with $[\text{Hg}(2\text{-C}_6\text{H}_4\text{NO}_2)_2]$ (1 : 2) to give metallic mercury and the complex $[\text{Rh}(2\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O})_2\text{Cl}(\text{CO})]$ whose crystal structure shows an octahedral co-ordination with one oxygen atom of each nitrophenyl ligand co-ordinated to the rhodium atom.

There are few reported *ortho*-nitrophenyl complexes mainly because of the instability of the corresponding organolithium derivative.¹ $[\text{Pd}(2\text{-C}_6\text{H}_4\text{NO}_2)\text{Cl}(\text{PPh}_3)_2]$ has been prepared by oxidative addition,² and $[\text{Hg}(2\text{-C}_6\text{H}_4\text{NO}_2)_2]$ has been used in preparations involving transmetallation.³ The oxidative addition route is limited to the preparation of halogenomonoaryl

derivatives of transition metals. We are developing the transmetallation route and have described mono- and di-aryl gold complexes³ which are not accessible *via* oxidative addition. In all the reported complexes the *ortho*-nitrophenyl group seems to act as a monodentate ligand.⁴ Herein we report our preliminary results obtained by applying the

organomercury route to the synthesis of a rhodium complex which is the first example of a cyclometalated *ortho*-nitrophenyl complex and also has interesting structural features.

The reaction (CH_2Cl_2 ; room temp.; 4 h) between $[\text{RhCl}(\text{CO})_2]_2$ and $[\text{Hg}(2\text{-C}_6\text{H}_4\text{NO}_2)_2]$ (1 : 2) gives metallic mercury and a solution from which the yellow $[\text{Rh}(2\text{-C}_6\text{H}_4\text{N}(\text{O})\text{O})_2\text{Cl}(\text{CO})]$ (1) may be isolated† in ca. 50% yield.

The crystal structure of (1) (Figure 1)‡ consists of discrete molecules linked by van der Waal's forces. The Rh atom displays a distorted octahedral co-ordination being linked to *cis* CO and chloro ligands. Both the carbon and the oxygen-donor atoms are also mutually *cis*.§ The Rh–C(*nx*), Rh–CO, and Rh–Cl bond distances are normal.⁸ The dihedral angles between the nitro and the phenyl groups are 9.4(4) and 1.3(4)° for the C(1*x*) and C(2*x*) nitrophenyl groups. This planarity allows strong electron delocalization which is clearly shown in the C–C bond distances of the phenyl rings [two short bonds: C(11)–C(16); C(13)–C(14); C(21)–C(22); C(24)–C(25), mean length 1.28(3) Å, and four long bonds, mean length 1.48(4) Å, with different distributions in the two rings]. Three of the N–O and the two N–C bond distances are significantly longer¶ [mean 1.33(4) Å] and shorter [mean 1.37(1) Å], respectively than those reported⁹ for some nitrophenolate complexes of Cu and Ru containing co-ordinated and unco-ordinated nitro groups (N–O: 1.22–1.23 Å; C–N: 1.43 and 1.46 Å) where such a delocalization is not present. In fact the foregoing nitrophenolate complexes show $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ vibrations at frequencies in the ranges expected for nitroaromatic groups (ca. 1550 and 1320 cm^{-1}) as is the case in the *ortho*-nitrophenyl gold complexes.³ Therefore the lowering of $\nu_{\text{asym}}(\text{NO}_2)$ observed in (1) (1270 cm^{-1}) is evidence for a cyclometalated *ortho*-nitrophenyl group.

† Complex (1) gave satisfactory elemental analyses, m.p. 212–214 °C; i.r. (CHCl_3) $\nu(\text{CO})$ 2096 vs; $\nu_{\text{asym}}(\text{NO}_2)$ 1525 and 1535 vs; $\nu_{\text{sym}}(\text{NO}_2)$ 1270 br., vs; $\nu(\text{Rh}-\text{Cl})$, 310s cm^{-1} ; m/z 410 (M^+ , 30%), 382 ($M^+ - \text{CO}$, 100), 347 ($M^+ - \text{CO} - \text{Cl}$, 44), 225 ($M^+ - \text{CO} - \text{Cl} - \text{C}_6\text{H}_4\text{NO}_2$, 41), and 103 (Rh^+ , 20).

‡ Crystal data: $\text{C}_{13}\text{H}_8\text{ClN}_2\text{O}_5\text{Rh}$; $M = 410.58$, triclinic, space group $P\bar{1}$, $a = 6.555(2)$, $b = 8.868(2)$, $c = 13.236(3)$ Å, $\alpha = 104.82(2)$, $\beta = 104.51(2)$, $\gamma = 83.88(2)^\circ$, $U = 719.3(5)$ Å³, $D_c = 1.89$ g cm^{-3} , $Z = 2$, $\lambda(\text{Mo}-K_\alpha) = 0.71069$ Å, $F(000) = 404$, $\mu(\text{Mo}-K_\alpha) = 13.63$ cm^{-1} ; room temperature; crystal dimensions $0.1 \times 0.1 \times 0.15$ mm; Enraf-Nonius CAD-4 diffractometer; graphite monochromatized Mo- K_α radiation; θ - 2θ technique. 2664 Reflections in the range $2 \leq \theta \leq 25^\circ$, 2140 observed [$I \geq 2.5\sigma(I)$]. Lorentz-polarization and absorption corrections were applied. The structure was solved by direct methods (MULTAN⁵). The structure was refined treating hydrogen atoms isotropically and the rest anisotropically by full-matrix least-squares methods, using SHELX 76,⁶ to a final R value of 0.037, R_w 0.36 [$w = (\sigma^2|F_o| + 0.0037|F_o|^2)^{-1}$]. f , f' , and f'' values were taken from ref. 7. Hydrogen atoms were not located. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The Rh, C(1), O(11), C(21), and O(21) atoms are roughly coplanar [maximum deviation from mean plane 0.052(5) Å for Rh]. The angles between this plane and the Cl–Rh and C(11)–Rh bonds are 84.8(2) and 80.0(2)°, respectively.

¶ The shortening of the N(2)–O(22) bond length can be explained by disorder of the second atom, as indicated by the thermal parameters.

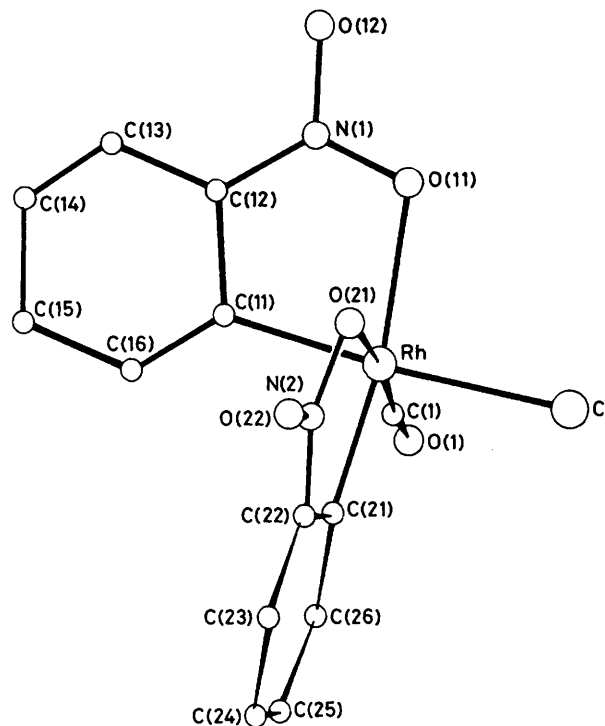


Figure 1. Molecular structure of complex (1). Important bond lengths (Å) and angles (°): Rh–Cl 2.416(1); Rh–C(1) 1.833(5); Rh–C(11) 2.041(3); Rh–O(11) 2.219(3); Rh–C(21) 1.984(4); Rh–O(21) 2.135(4); O(1)–C(1) 1.096(6); N(1)–C(12) 1.378(5); N(1)–O(11) 1.283(5); N(1)–O(12) 1.321(4); N(2)–C(22) 1.362(5); N(2)–O(21) 1.375(5); N(2)–O(22) 1.171(6) Å; O(12)–N(1)–O(11) 111.0(3); O(22)–N(2)–O(21) 119.2(4).

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