

Preliminary communication

RAPID INTRAMOLECULAR INTERACTIONS BETWEEN ORGANIC ISOCYANATES AND HEXAFLUOROBUT-2-YNE ON A DIRHODIUM CENTRE; X-RAY CRYSTAL STRUCTURE OF $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\mu_2(\eta^3\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{C}(\text{O})\text{N}(\text{Ph}))\}$

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Summary

Complexes of formula $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\text{CF}_3\text{C}_2\text{CF}_3 \cdot \text{RNCO}\}$ have been prepared by three methods, from reactions between organic isocyanates and $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ or $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$; by treatment of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)$ with organic azides; and by oxidation with Me_3NO of the organic isocyanide in $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})\text{-(CNR)}(\text{CF}_3\text{C}_2\text{CF}_3)$. The crystal and molecular structure of the complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\text{CF}_3\text{C}_2\text{CF}_3 \cdot \text{RNCO}\}$ with $\text{R} = \text{Ph}$ has been determined from single crystal X-ray diffraction data. This reveals that the isocyanate has condensed with the hexafluorobut-2-yne to form an amide ligand of the form $\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{C}(=\text{O})\text{N}(\text{R})$; this bridges the two rhodium atoms in a $\mu_2 \eta^3$ -manner.

Organic isocyanates, $\text{RN}=\text{C}=\text{O}$, are industrially important organic chemicals; they are condensed with dihydroxy compounds to produce polyurethanes. Although soluble metal complexes are used in the formation of $\text{RN}=\text{C}=\text{O}$ compounds and, in some instances, to accelerate their conversion to polyurethanes, little is known about organic isocyanates as ligands. Among the few known $\text{M}(\text{RNCO})$ complexes are those of ruthenium [1], rhodium [2,3], iridium [4], and nickel [5]. To the best of our knowledge, there are no examples of the coordination of organic isocyanates to a dimetal centre.

We have investigated three alternative routes to the formation of organic

isocyanate-dirhodium complexes. They involve (i) the direct coordination of $\text{RN}=\text{C}=\text{O}$ to a coordinatively-unsaturated Rh_2 centre, (ii) the addition of nitrenes to coordinated CO, and (iii) the oxidation of coordinated isocyanides. In this communication, we present a preliminary account of our synthetic studies and a brief description of the crystal and molecular structure of one of the products.

Treatment of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})\{\mu(\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)\}$ (I) [6] with $\text{RN}=\text{C}=\text{O}$ ($\text{R} = \text{Me}, \text{Bu}^t, p\text{-MeC}_6\text{H}_4$) in dichloromethane or tetrahydrofuran results in loss of CO and formation of the complexes $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\text{CF}_3\text{C}_2\text{CF}_3 \cdot \text{RNCO}\}$ (II). The reactions proceed at room temperature over several days or more rapidly in refluxing solvents. The complexes II were also obtained when $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2\{\mu(\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\}$ was treated with excess $\text{RN}=\text{C}=\text{O}$ at 120°C for 24 h. Generally, the yields of II obtained from these reactions were in the range 20–50%; other products that are formed in the reactions have not been fully characterized.

In the reaction of I with organic azides $\text{RN}=\text{N}^+\text{N}^-$ ($\text{R} = \text{Ph}, \text{PhCO}, p\text{-MeC}_6\text{H}_4\text{SO}_2$) in diethyl ether at room temperature, there is immediate evolution of N_2 and formation of the complexes II in 85–95% yields. Presumably, these complexes are formed via a nitrene species of the type $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{NR})(\text{CF}_3\text{C}_2\text{CF}_3)$, but these intermediates have not been isolated. Related carbene complexes $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CRR}')(\text{CF}_3\text{C}_2\text{CF}_3)$ have been characterized recently [7].

Isocyanide complexes $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\text{CNR})(\text{CF}_3\text{C}_2\text{CF}_3)$ can be obtained [6] from I and $:\text{C}\equiv\text{NR}$ (e.g. $\text{R} = \text{Me}, \text{Bu}^t, \text{Pr}^i, \text{C}_6\text{H}_{11}$). When these complexes are treated in acetone at 95°C with the mild oxidant Me_3NO , II is formed in 25–30% yields. Thus, there has been oxygen-transfer from Me_3NO to the CNR ligands, with subsequent retention of RNCO in the organo-metallic products. In the reaction with the $\text{CNC}_6\text{H}_{11}$ complex, some CO_2 is evolved; however, no CO_2 is detected in the gaseous products from the CNBu^t system.

All of the complexes II are air stable, orange-red to crimson solids. They have been obtained analytically pure, and the main features of their spectroscopic properties are similar. The mass spectra show intense peaks for the parent ion $(P)^+$ and for $(P - \text{RNCO})^+$. In the IR spectra, a band near 1700 cm^{-1} (e.g. at 1680 and 1690 cm^{-1} when $\text{R} = \text{Ph}$ and Bu^t , respectively) is presumably associated with the $\text{C}=\text{O}$ part of the ligand. In the ^1H NMR spectra, there are two C_5H_5 resonances (e.g. at δ 5.22 and 5.17 ppm, doublets, $J(\text{RhH})$ 1 Hz for II, $\text{R} = \text{Ph}$); two CF_3 resonances are observed in the ^{19}F spectra (e.g. at δ 46.9 and 56.2 ppm, quartets, $J(\text{FF})$ 12 Hz for (II, $\text{R} = \text{Ph}$)). These results are consistent with any attachment of the RNCO ligand which leads to inequivalence of the two 'halves' of the molecule.

In an attempt to identify the mode of attachment of the isocyanate ligand in II ($\text{R} = \text{PhCO}$), the ^{13}C NMR spectrum was investigated. In the natural abundance spectrum with no relaxation reagent present, peaks due to phenyl carbons (at δ 133.6, 131.5, 130.5 and 128.3 ppm) and the cyclopentadienyl carbons (at δ 85.2 and 82.8 ppm, doublets, $J(\text{RhC})$ 6 Hz) were observed. With samples prepared from ^{13}CO -enriched I, and with added $\text{Cr}(\text{acac})_3$, extra signals were detected at δ 178.5 (weak) and 166.4 ppm (strong). The former

is attributed to the acyl carbon of the benzoyl group (PhC(=O)N=); the latter is also consistent with an acyl-type C adjacent to a N atom (RNC(=O)-). However, considerable uncertainty remains about the nature of the ligand and its mode of attachment to the dirhodium centre. Consequently, a single crystal X-ray study was undertaken for the complex with $\text{R} = \text{Ph}$.

Crystal data: $\text{C}_{21}\text{H}_{15}\text{F}_6\text{NORh}_2$, $M = 617.2$, tetragonal, space group $I4_1/a$ (C_6^4h , No. 188), a 24.49(1), c 14.298(4) Å, U 8577(6) Å³, D_c ($Z = 16$) 1.91 g cm⁻³, $F(000) = 4800$.

Single crystal X-ray diffraction data was measured to $2\theta_{\text{max}} = 50^\circ$ with a

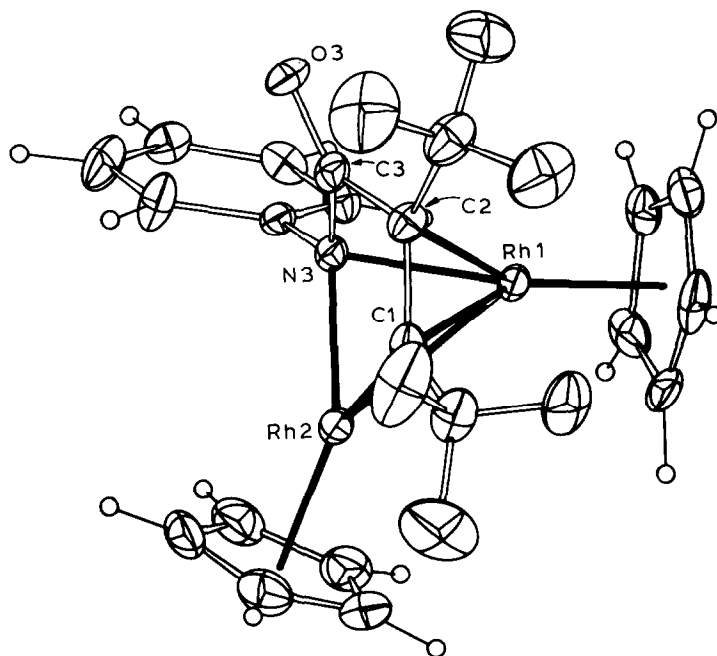


Fig. 1. Molecular structure of $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2[\mu_2(\eta^3\text{-C(CF}_3\text{)}_2\text{C(CF}_3\text{)C(O)N(Ph)})]$. Bond lengths: Rh(1)–Rh(2) 2.612(1), Rh(1)–C(1) 2.020(9), Rh(2)–C(1) 2.148(8), Rh(1)–C(2) 2.138(8), Rh(1)–N(3) 2.169(6), Rh(2)–N(3) 2.049(6), C(1)–C(2) 1.45(1), C(2)–C(3) 1.48(1), C(3)–O(3) 1.20(1), C(3)–N(3) 1.41(1) Å.

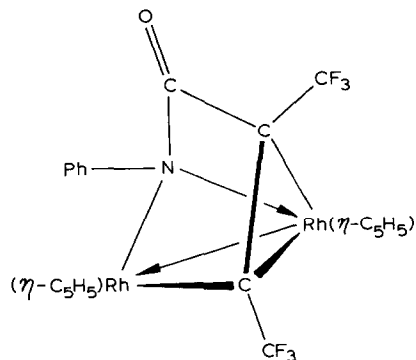
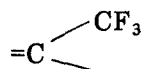


Fig. 2. Coordination mode of the bridging ligand in the complex $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2[\mu_2(\eta^3\text{-C(CF}_3\text{)}_2\text{C(CF}_3\text{)C(O)N(R)})]$.

Syntex P2₁ four-circle diffractometer in conventional $2\theta/\theta$ scan mode with graphite monochromated Mo- K_α radiation. For 2559 unique reflections ($I > 3\sigma(I)$) R is 0.046*. A representation of the molecular structure, and some selected bond parameters, are given in Fig. 1. The structure reveals that the cyanate-carbon has condensed with a carbon of hexafluorobut-2-yne to generate a bridging amide ligand of the type $C(CF_3)C(CF_3)C(=O)N(Ph)$. The coordination-mode is represented in Fig. 2.

The reactions reported in this communication establish that the $RN=C=O$ group is highly reactive towards unsaturated carbon atoms of the type



Although intermediates are presumably formed in which a recognizable 'RNCO ligand' is present, no evidence for these species was actually obtained. Further investigation of the formation and reactions of these complexes is underway. It is hoped that this will provide clues to the reaction pathways followed in metal catalyzed cocyclization of acetylenes with organic isocyanates, see, for example, the cobalt catalyzed formation of 2-pyridones [8].

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References

- 1 S. Cenini, M. Pizzotti, F. Porta and G. La Monica, *J. Organomet. Chem.*, **88** (1975) 237.
- 2 S. Hasegawa, K. Itoh and Y. Ishii, *Inorg. Chem.*, **13** (1974) 2675.
- 3 H.L.M. van Gaal and J.P.J. Verlaan, *J. Organomet. Chem.*, **133** (1977) 93.
- 4 J.P. Collman, M. Kubota, F.D. Vastine, J.Y. Sun and J.W. Kang, *J. Am. Chem. Soc.*, **90** (1968) 543.
- 5 S. Otsuka, A. Nakamura and Y. Tatsuno, *J. Am. Chem. Soc.*, **91** (1969) 6994.
- 6 R.S. Dickson, A.P. Oppenheim and G.N. Pain, *J. Organomet. Chem.*, **224** (1982) 377.
- 7 R.S. Dickson, G.D. Fallon, R.J. Nesbit and G.N. Pain, *J. Organomet. Chem.*, **236** (1982) C61.
- 8 P. Hong and H. Yamazaki, *Tetrahedron Lett.*, (1977) 1333.

*Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full literature citation for this communication.