Journal of Organometallic Chemistry, 268 (1984) C43–C47
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REDUCTION PRODUCTS OF DINUCLEAR [$Rh_2Cl_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$]. CRYSTAL STRUCTURE OF [$Rh_2HgCl(\mu\text{-}H)(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$]

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(Received March 21st, 1984)

Summary

Treatment of [$Rh_2Cl_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$] with various reducing agents gives a number of products, the type depending on the conditions employed. The products isolated include [$Rh_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$], [$Rh_2(CO)_3\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$], and [$Rh_2HgCl(\mu\text{-}H)(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$]; the structure of the last complex was determined by X-ray diffraction.

It has previously been reported that reduction of [$Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2$] with $NaBH_4$ affords the dinuclear rhodium(0) compound [$Rh_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2$] and that the latter reacts readily with carbon monoxide to produce a tricarbonyl derivative [$Rh_2(\mu\text{-}CO)(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2$] (I) containing a bridging as well as terminal carbonyl groups [1].

In a related study we established that [$Rh_2Cl_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$] can also be reduced, and that in the presence of carbon monoxide this reduction affords a tricarbonyl product of stoichiometry [$Rh_2(CO)_3\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2$] (II) which, in contrast to the $Ph_2PCH_2PPh_2$ derivative, contains terminal carbonyls only [2].

With the object of synthesising directly dinuclear analogues of Wilkinson's hydroformylation catalyst [$RhH(CO)(PPh_3)_3$], we have now investigated the re-

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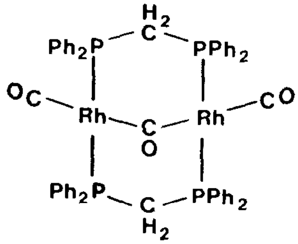
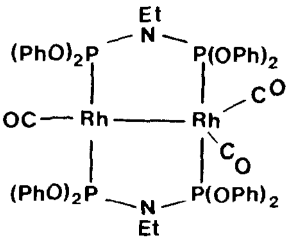


(I)



(II)

duction of $[Rh_2Cl_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ under an atmosphere of dihydrogen. Using amalgamated zinc as reductant we have obtained a product with elemental analysis consistent with the formulation $[Rh_2HgHCl(CO)_2\cdot\{(PhO)_2PN(Et)P(OPh)_2\}_2]$; its infrared spectrum exhibited C—O stretching peaks corresponding to terminal carbonyls only $\{\nu$(C—O): 1995sh and 1983s (mull); 1980 cm^{-1} $(CH_2Cl_2)\}$. Because it was expected that the compound would have an unusual structure an X-ray diffraction study was undertaken.

Crystal data: $C_{54}H_{51}ClHgN_2O_{10}P_4RH_2$, M = 1452.6; triclinic, space group $P\bar{1}$, a 13.562(6), b 12.303(5), c 18.990(8) Å, α 97.5(2), β 76.9(2), γ 115.8(2)°, U 2776 $Å^3$, D_m 1.72, D_c 1.74 g cm^{-3}, Z = 2, $\mu(Mo\text{-}K_\alpha)$ 33.8 cm^{-1}. Diffraction data were collected in the $\omega - 2\theta$ mode on a Philips PW 1100 four-circle diffractometer. The structure was solved by conventional Patterson and difference Fourier methods and refined by a blocked-matrix least squares procedure to an R value of 0.057 for 7576 independent reflections $\{I > 2\sigma(I)\}$*.

The molecular stereochemistry of the compound is illustrated in Fig. 1. The rhodium and mercury atoms adopt a triangular structure with the rhodium—rhodium and rhodium—mercury distances corresponding to those normally associated with formal rhodium—rhodium and rhodium—mercury bonds (Rh(1)—Rh(2) 2.762(1), Rh(1)—Hg 2.711(1) and Rh(2)—Hg 2.778(1) Å). The rhodium—rhodium edge is bridged by the two diphosphazane ligands *trans* disposed with respect to each other. The carbonyl groups are terminally coordinated and are essentially colinear with the rhodium—rhodium vector (Rh(1)—Rh(2)—C(2) = Rh(2)—Rh(1)—C(1) = 173.3(4)°) and coplanar with the chlorine, the mercury and the two rhodium atoms with the angle between the least squares plane for these atoms and that for the $Rh_2P_4N_2(CO)_2$ system being 89.6°. The two RhPNPRh five-membered rings are slightly puckered with ring A {N(1)—P(1)—Rh(1)—Rh(2)—P(3)} being more so than ring B {N(2)—P(2)—Rh(1)—Rh(2)—P(4)} (Q: ring A, 0.29; ring B, 0.16)**. Both rings have hybrid envelope-twist conformations (conformation: ring A, $_{Rh(2)}E + {}^{Rh(1)}_{Rh(2)}T$ (2/1); ring B, $_{P(4)}E + {}^{Rh(2)}_{P(4)}T$ (1/1)} with ring A having more envelope character (± 70%). The mole-

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*The 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.

**The puckering parameters were calculated by the method of Cremer and Pople [3] while Altona and Sundaralingam's [4] nomenclature is used to describe the conformations.

cule contains a near-plane of symmetry through the mercury, the chlorine and the two nitrogen atoms as well as through the carbon atoms of the ethyl groups. The two nitrogen atoms are effectively sp^2 hybridised with the two P—N—P bond angles being close to 120° (P(1)—N(1)—P(3) 117.9(4)°; P(2)—N(2)—P(4) 118.7(4)°) and the methylene carbons of the two ethyl groups being essentially coplanar with the two PNP planes (distance of C(27) from P(1)N(1)P(3) plane 0.25(1) Å; distance of C(41) from P(2)N(2)P(4) plane 0.11(1) Å).

To account for the diamagnetism the molecule must contain a hydridic ligand.

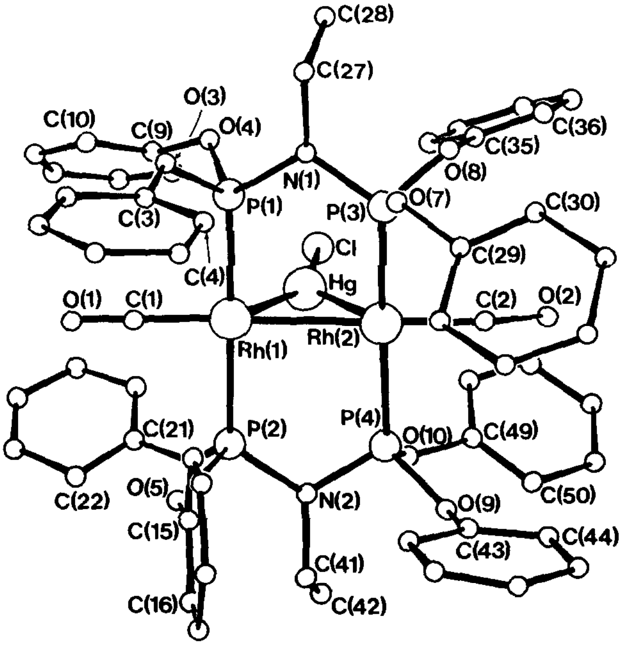


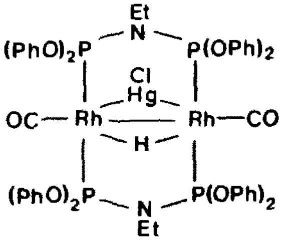
Fig. 1. The molecular structure of [$Rh_2HgCl(\mu_2$-H)(CO)$_2$ {μ-(PhO)$_2$PN(Et)P(OPh)$_2$}$_2$] (with omission of the μ-H). Some relevant interatomic distances and angles: Rh(1)—Rh(2), 2.762(1); Rh(1)—Hg, 2.711(1); Rh(2)—Hg, 2.778(1); Rh(1)—P(1), 2.253(2); Rh(1)—P(2), 2.254(2); Rh(2)—P(3), 2.242(2); Rh(2)—P(4), 2.257(2); Hg—Cl, 2.470(3) Å; Rh(1)—Hg—Rh(2), 60.4(0); Rh(1)—Rh(2)—Hg, 58.6(0); Rh(2)—Rh(1)—Hg, 61.0(0); P(1)—Rh(1)—Rh(2), 91.1(1); P(2)—Rh(1)—Rh(2), 91.2(1); P(3)—Rh(2)—Rh(1), 90.1(1); P(4)—Rh(2)—Rh(1), 91.4(1); Rh(1)—Rh(2)—C(2), 173.3(4); Rh(2)—Rh(1)—C(1), 173.3(4); Rh(1)—Hg—Cl, 153.3(1); Rh(2)—Hg—Cl, 145.4(1); P(1)—N(1)—P(3), 117.9(4); P(2)—N(2)—P(4), 118.7(4)°.

This possibility was investigated using a 500 MHz NMR spectrometer and, indeed, as well as resonances at 7.41 to 6.92 ppm, a multiplet centred at 3.82 ppm and a triplet at 1.35 ppm, corresponding to the phenyl, methylene and methyl hydrogens respectively, an 11-line multiplet centred at −12.03 ppm and readily assigned to an edge-bridging hydridic ligand was observed in the ^{1}H NMR spectrum. Undoubtedly the hydride bridges the two rhodium atoms.

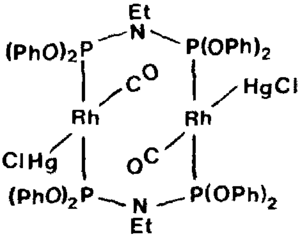
An alternative to regarding this molecule as a triangular cluster of mercury and rhodium is to consider it to be a dinuclear compound of rhodium in which the two rhodium atoms are not only bridged by a hydridic and two diphosphazane ligands but also by a HgCl group. In either description however the

HgCl moiety contributes both a single electron and a single orbital to the skeletal bonding. This investigation, together with a number of others [5—9], reveals that, similar to gold [10—20], mercury can also be incorporated into metal cluster compounds and, again, either across an edge or over a face of a cluster.

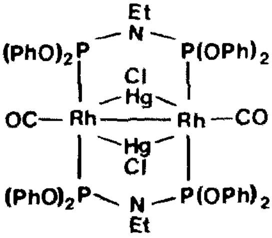
Although the actual mechanism for the formation of $[Rh_2HgCl(\mu_2\text{-}H)(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ (III) cannot be ascertained from the experimental data available, it is apparent that the reduction of $[Rh_2Cl_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ by amalgamated zinc is accompanied by the effective insertion of mercury into a rhodium—chlorine bond. To establish whether the parent compound itself is susceptible to mercury insertion it was treated with mercury, and the rapidly-formed product was indeed found to be $[Rh_2(HgCl)_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$. Although spectroscopic evidence cannot readily distinguish between structures IV and V, the yellow colour of the compound favours structure IV.



(III)

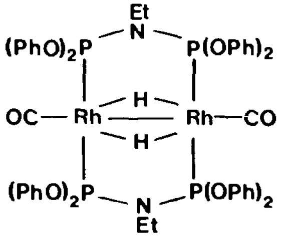


(IV)



(V)

In the light of the formation of III, $[Rh_2Cl_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ was treated under hydrogen with the non mercury-containing reductant sodium naphthalide with a view to synthesising $[Rh_2(\mu\text{-}H)_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ (VI). A new product was formed but mixed with the tricarbonyl $[Rh_2(CO)_3\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ (II) from which it could not be separated. However on the basis of its ready reaction with CO to produce II and the frequency of its C—O stretching mode (vide infra) it was identified as $[Rh_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ (VII). Not surprisingly, compounds II and VII were also produced in the corresponding reduction under nitrogen.



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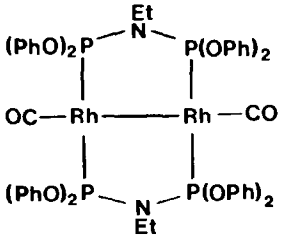

(VII)

Direct synthesis of $[Rh_2(CO)_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$ (VII) was achieved by treatment of the tricarbonyl II with trimethylamine oxide in THF under reflux. The compound, which exhibits a single C—O stretching peak at 1972 cm^{-1} in its cyclohexane solution IR spectrum, was found to be highly reactive and as a consequence could not be isolated sufficiently pure for characterisation purposes. Its identification was based on quantitative regeneration of compound II on treatment with carbon monoxide. It is highly reactive to a wide range of nucleophiles and electrophiles including alkynes, tertiary phosphines and phosphites, halogens, protons, carbonium ions, carbon disulphide and carbon dioxide, but not hydrogen.

Acknowledgements. The authors thank the South African Council for Scientific and Industrial Research and the University of Natal for financial support, Mr. J. Albain, N.P.R.L., C.S.I.R., Pretoria, for the measurement of the intensity data and Johnson Matthey Limited for the loan of rhodium salts.

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