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Rhodium(I) Complexes with Thioethers, Dithioethers or Phosphinoalkylthioethers

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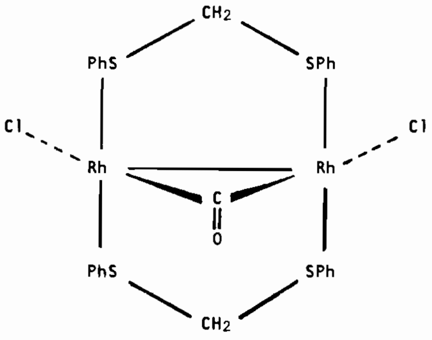
Complexes of platinum-group metals with bidentate ligands are of increasing interest structurally and as catalysts for hydrogenation, hydroformylation, and related processes [*e.g.*, 1–6]. Complexes in which one ligand is significantly more labile than another are potentially more stable than complexes with multiple labile ligands, and more catalytically active than complexes with multiple strongly bound ligands [7]. Consequently, we have investigated the synthesis and reactivity of a series of complexes of PhSMe, Ph_2S, $PhS(CH_2)_nSPh$ (I(*n*); *n* = 1–6), $PhS(O)CH_2S(O)Ph$, and $Ph_2P(CH_2)_mSPh$ (II(*m*); *m* = 1–3). The ligand II (*1*) is entirely novel, and was synthesised by the reaction of $KPPh_2$ with $PhSCH_2Cl$ in tetrahydrofuran.

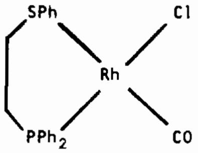
Reaction of a dithioether with a solution of $[Rh_2Cl_2(CO)_4]$ (Rh: I(*n*) = 2) under an atmosphere of CO frequently gives a product which is an oil or waxy solid, and which is very sensitive to air, moisture, and heat. Only the complexes with I(*2*) or I(*4*) give hard, well-formed crystals. The orange to dark-red complexes are characterised by carbonyl bands in the infra-red spectrum close to 2070 and 2000 cm^{-1}, thus indicating that the products are dicarbonyl, *cis*-square-planar complexes with brigding dithioether ligands, $RhCl(CO)_2 \cdot SPh(CH_2)_nSPh \cdot RhCl(CO)_2$[*]. Similarly, thioethers can form complexes *cis*-$[RhCl(CO)_2 \cdot SR_2]$. Under an atmosphere of CO the carbonyl ligands exchange rapidly. The complex $[RhCl(CO)_2(PhSMe)]$ with ^{13}CO (90% enriched) shows only one Rh–^{13}CO resonance (δ = 180.3 p.p.m. *vs.* TMS) at temperatures greater than 230 K, but two environments for ^{13}CO at 190 K (δ = 178.6 and 182.2 p.p.m.) [8].

Under an atmosphere of dinitrogen and with stoicheiometry (I(*n*): Rh = 1), reaction of a solution of I(*n*) in benzene with a solution of $[Rh_2Cl_2(CO)_4]$ in hexane normally gives the *trans*, dinuclear, dithioether-bridged complex $[RhCl(CO)\{I(n)\}]_2$ as a light brown powder. The assignment of the above structure is based on elemental analyses and the infra-red spectra[**]. The complexes are characterised by carbonyl bands in the infra-red spectrum close to 1960 cm^{-1}, and Rh–Cl bands close to 300 cm^{-1}, in each case comparable with the spectral characteristics of the analogous *trans*, diphosphine-bridged complexes [9].

A subsequent reaction of $[Rh_2Cl_2(CO)_4]$ with I(*1*) is unique within this series. When dinitrogen is bubbled through an acetone solution of $[RhCl(CO)\{I(1)\}]_2$, a green complex is formed. This complex has a single carbonyl band in the infra-red spectrum at 1820 cm^{-1}. The elemental analyses are consistent with the formulation $[Rh_2Cl_2(\mu\text{-}CO)(PhSCH_2SPh)_2]$, (*A*)[†]. This complex therefore represents the first example of an 'A-frame' complex containing thioether ligands, and is analogous to recently reported complexes of rhodium with diphosphine or diarsine ligands [10].



A



B

By comparison with a recent determination by Roundhill [11] of the structure of an iridium complex chelated by a phosphinoarylamine ligand, the

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[*] *e.g.* $[Rh_2Cl_2(CO)_4\{I(2)\}]$, *Anal.* Found: C, 33.98; H, 2.08; Cl, 11.12; S, 9.99%. Calcd: C, 34.04; H, 2.22; Cl, 11.16; S, 10.10%.

[**] *e.g.* $[RhCl(CO)\{I(6)\}]_2 \cdot C_6H_6$, *Anal.* Found: C, 52.85; H, 4.98; Cl, 6.67; S, 12.50%. Calcd: C, 52.02; H, 4.96; Cl, 6.98; S, 12.62%.

[†] *Anal.* Found: C, 41.93; H, 3.12; Cl, 9.05; S, 16.60%. Calcd: C, 42.15; H, 3.14; Cl, 9.22; S, 16.67%.

yellow, chelated complex of ligand II (*2*) [12], [RhCl(CO)($Ph_2PCH_2CH_2SPh$)], is assigned structure (*B*). The carbonyl band (2000 cm^{-1}) is of similar value to that of [RhCl(CO)($Ph_2PCH_2CH_2PPh_2$)] [9] or [RhCl(CO)($Ph_2PC_6H_4NMe_2$)] [11]. With stoicheiometry II(*2*): Rh $\geqslant$ 2 the complex product is not an electrolyte in solution in acetone, is characterised by an infra-red carbonyl band at 1963 cm^{-1} and is therefore assigned the structure *trans*-[RhCl(CO){II(*2*)}$_2$], in which the ligand is coordinated by the phosphorus atom only. The ligand Ph_2PCH_2SPh, II(*1*), also forms a complex of the latter stoicheiometry. However, no chelate complex analogous to *B* has yet been synthesised. The reaction of [$Rh_2Cl_2(CO)_4$] with II(*1*) (Rh: II(*1*) = 1) in dichloromethane affords a mixture of *trans*-[RhCl(CO){II(*1*)}$_2$] and starting material.

The complexes [$Rh_2Cl_2(CO)_4${I(*n*)}] are catalytically active for a brief time for the hydrogenation of olefins, but then decompose under hydrogenation conditions [13]. The complex [RhCl(CO){II(*2*)}$_2$] is inactive at low temperatures and pressures.

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