Rhodium(III) Alkyls Stabilized by a Quadridentate Schiff-base Ligand

By R. J. COZENS, K. S. MURRAY, and B. O. WEST*

(*Department of Chemistry, Monash University, Clayton, Victoria, Australia* 3168)

Summary RhCl(salen)(py) is reduced by sodium amalgam or $NaBH_4$ in alkaline solution to give compounds which react with alkyl halides to yield the alkyls RhR(salen)(py) (R = Me or Et); reduction of the chloro-complex with zinc amalgam gives a compound believed to be the metal-metal-bonded dimer $[Rh(salen)(py)]_2$.

STABLE Co^{III} alkyl and aryl derivatives have been prepared using quadridentate Schiff bases as stabilizing ligands.[1-4] We now report the first syntheses of analogous Rh^{III} derivatives containing the *NN'*-ethylenebis(salicylideneiminato) group (salen).

The ligand does not readily co-ordinate with Rh^{III} species because of the inertness of the aquo- or other groups attached to the ion. However, as for other Rh^{III} compounds,[5] in the presence of a suitable reducing agent, complex formation can be achieved. Thus a deep red solution of hydrated rhodium(III) chloride and the Schiff base in methanolic pyridine is reduced by 5% zinc amalgam to give a pale yellow solution. Careful evaporation of the solution yields a yellow compound, insoluble in most solvents, whose analytical composition corresponds to Rh(salen)(py). The complex has an i.r. spectrum indicative of the co-ordinated ligand and there is no evidence of a Rh–H absorption in the range 1800—2200 cm^{-1}. It does not react with methyl iodide at 120° in a sealed tube. The complex is probably a dimer with Rh–Rh bonds comparable to the Rh–dimethylglyoxime derivative recently described.[6,7]

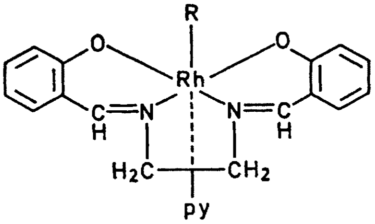
An alternative reaction is obtained when hydrated rhodium(III) chloride followed by zinc dust is added to a solution of the ligand in hot pyridine. The yellow crystalline compound RhCl(salen)(py) precipitates and can be recrystallized from pyridine.

The complex does not react with MeMgI in ether suspension. However, a suspension of the chloro-compound in dry, degassed tetrahydrofuran reacts rapidly with 0·2% sodium amalgam yielding a deep green-black solution, stable only in the absence of air. Addition of methyl iodide or ethyl bromide to the solution gave an orange colour and after pyridine followed by water had been added, the Rh^{III}-alkyl compound RhR(salen)(py) (R = Me or Et) crystallized from solution.

Treatment of RhCl(salen)(py), suspended in aqueous methanol containing 15% (w/v) sodium hydroxide, with $NaBH_4$ in the presence of $PdCl_2$ catalyst gives a red-brown air-sensitive solution which reacts with alkyl halides (MeI or EtBr) to yield the same orange alkyl derivatives RhR(salen)(py), which can be precipitated by water after the addition of further pyridine to the system.

The constitution of the two reduced Rh species described is currently under investigation. Weber and Schrauzer[8] have recently described the reduction of Rh^{III} dimethylglyoxime derivatives by BH_4^- ions and postulate the formation of red-brown Rh^I species $[Rh(DMG)_2]^-$ in strongly alkaline solution which react with alkyl halides to give organo-rhodoxime compounds.

The ^1H n.m.r. spectra of the RhR(salen)(py) compounds in $(CD_3)_2SO$ show a characteristic splitting of the alkyl group resonances (CH_3 or CH_2 of C_2H_5) due to ^{103}Rh–H coupling which confirms the constitution of the complexes as Rh–C bonded derivatives. [Rh–CH_3: δ 1·3 (J_{Rh-H} *ca.* 3Hz); Rh–C_2H_5: δ 0·78 (J_{H-H} 7Hz, CH_3) and 2·31 (J_{Rh-H} *ca.* 3Hz, CH_2)]. The δ values of the ligand and attached alkyl group protons show significant shifts compared to those of CoR(salen) derivatives, *e.g.* CoMe(salen)(py),[3] δ = 2·22 (CH_3); CoEt(salen)(py),[9] δ = −0·06 (CH_3) and 3·34 (CH_2). In view of the known tendency for Co^{III}R(salen)L complexes to exist in the *trans*-form,[10] it seems reasonable to postulate a similar structure for the Rh complexes (Figure). The Rh compounds are notably less sensitive to light than their cobalt analogues.



FIGURE

(*Received, July 20th,* 1970; *Com.* 1193.)

---

[1] G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organometallic Chem.*, 1966, **6**, 181.
[2] G. Costa, G. Mestroni, and L. Stefani, *J. Organometallic Chem.*, 1967, **7**, 493.
[3] C. Floriani, M. Puppis, and F. Calderazzo, *J. Organometallic Chem.*, 1968, **12**, 209.
[4] G. N. Schrauzer, J. W. Sibert, and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1968, **90**, 6681.
[5] R. G. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1965, 1951.
[6] S. A. Shchepinov, E. R. Sal'nikova, and M. L. Khidekel, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 2128.
[7] K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, 1969, **91**, 6517.
[8] J. H. Weber and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1970, **92**, 726.
[9] H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni, and G. Costa, *J. Organometallic Chem.*, 1968, **11**, 167.
[10] M. Cesari, C. Neri, G. Perego, E. Perrotti, and A. Zazzetta, *Chem. Comm.*, 1970, 276, and references therein.