

Preparation of Bis(*cis*-diacetyltetracarbonylrhenium)copper¹

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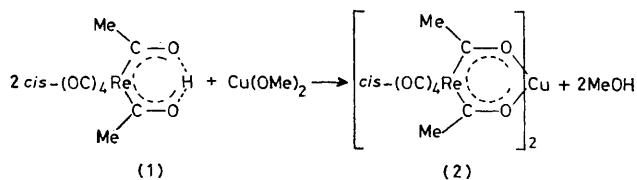
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Summary Treating the rhenium metalla-acetylacetonate complex (1) with a stoichiometric amount of anhydrous copper methoxide in dry diethyl ketone affords the first example of a metalla-acetylacetonate complex of a transition metal.

PREVIOUS studies² have demonstrated the preparation of several metalla-analogues of the β -diketonate anions, and the co-ordination of these organometallic anions to either aluminium(III) or gallium(III) ions affording neutral, tris-chelate complexes. These metalla-ligands represent the formal replacement of the methine group of a β -diketonate anion by an organometallic complex of a transition metal.

However, repeated attempts to synthesize complexes of these ligands which contain transition metal ions as the central co-ordinating metal have failed. These reactions always involved the formal displacement of an anion, such as a halide, from the transition metal ion by the anionic organometallic ligand. We report the successful preparation of a metalla-acetylacetonate complex of copper by the

formal elimination of methanol by treating the rhenium-enol complex (1) with anhydrous copper(II) methoxide³ in diethyl ketone at 25 °C as shown in the Scheme.



SCHEME

The bis-chelate copper complex (2) is isolated from toluene solution in 18% yield as a deep-red crystalline solid, m.p. 120–121 °C, and analysed satisfactorily for C, H, and Cu. Compound (2) is stable in air for at least four weeks, and is soluble in hexane, benzene, and polar organic solvents. The i.r. spectrum in hexane solution shows four terminal carbonyl stretching vibrations which are consistent with the

geometry at the rhenium centres: 2088m, 1991s, 1973vs, and 1965s cm^{-1} . A band of medium intensity at 1506 cm^{-1} is assigned to the ligand acyl C–O stretching vibration.

The magnetic moment [μ_{eff} (295 K)], of (2) as measured using a Faraday balance, is 1.76 BM which is within the range expected for d^9 -copper complexes having one unpaired electron.⁴ The e.s.r. spectrum at both 298 and 107 K indicates a square-planar co-ordination about the copper atom with values for g_{\parallel} and g_{\perp} of 2.21 and 2.09, respectively. The corresponding values for $\text{Cu}(\text{acac})_2$ are 2.26 and 2.04 respectively.⁵ The splitting due to the copper nuclear spin was not observed. A dilution study is being attempted with the hope of observing a hyperfine interaction with the rhenium nuclei. The red colour of (2) is explained by the

presence of three intense electronic absorptions in the near-u.v. region at 293 ($\log \epsilon$ 3.87), 405 (3.59), and 435 (3.60) nm (chloroform solution).

Preliminary results indicate that it is possible to prepare a neutral, tris-chelate iron(III) complex by treating (1) with anhydrous iron ethoxide. Also, the bis-chelate complex of zinc(II) results from treating (1) with diethylzinc apparently by the elimination of ethane.

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¹ See D. T. Hobbs and C. M. Lukehart, *J. Amer. Chem. Soc.*, 1977, **99**, 8357, for previous papers in this series.

² C. M. Lukehart and J. V. Zeile, *J. Amer. Chem. Soc.*, 1977, **99**, 4368; C. M. Lukehart, G. P. Torrence, and J. V. Zeile, *Inorg. Chem.*, 1976, **15**, 2393; *J. Amer. Chem. Soc.*, 1975, **97**, 6903.

³ C. H. Brubaker, Jr. and M. Wicholas, *J. Inorg. Nuclear Chem.*, 1965, **27**, 59.

⁴ F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 916.

⁵ H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, 1962, **36**, 3221.