

Preliminary communication

REACTIONS OF COORDINATED MOLECULES

XXI*. THE PREPARATION OF MIXED-LIGAND PARAMAGNETIC COMPLEXES CONTAINING METALLA- β -DIKETONATE LIGANDS

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Summary

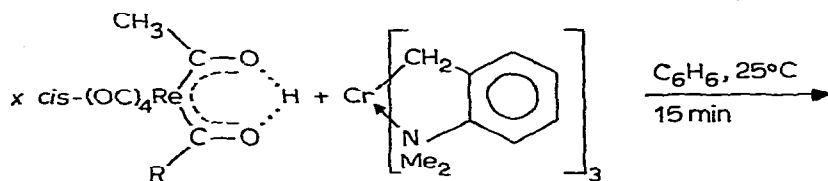
When tris(*N,N*-dimethyl-*o*-toluidyl)chromium or bis(acetylacetonato)copper are treated with metalla- β -diketones, a ligand exchange reaction occurs affording mixed-ligand transition metal complexes containing metalla- β -diketonate ligands. All of these complexes are polynuclear, paramagnetic molecules, and the chromium complexes possess either one or two chromium to carbon bonds.

We recently reported the successful preparation of the rhenaacetylacetonate complexes of copper(II), iron(III) and zinc(II) by treating $\text{Cu}(\text{OMe})_2$, $\text{Fe}(\text{OEt})_3$ and Et_2Zn with the stoichiometric amount of the rhenaacetylacetonate molecule. The ligand-exchange reaction apparently involves the formal elimination of alcohol or ethane [2]. We wish to report the extension of this synthetic method to include the first preparation of metalla- β -diketonate complexes of the transition metals containing other ancillary ligands. All of the polynuclear molecules reported here are paramagnetic, and in several complexes the ancillary groups include chelating benzylic ligands. There is considerable recent interest in the synthesis of thermally stable, paramagnetic complexes which contain metal to carbon bonds [3].

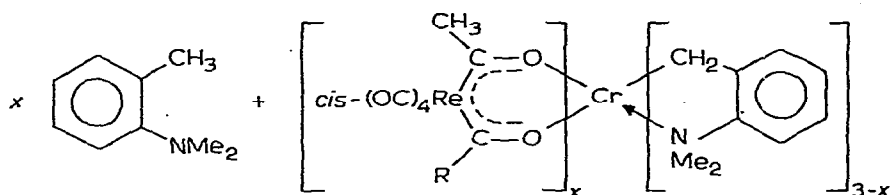
The new mixed-ligand rhenaa- β -diketonate complexes are prepared as in Scheme 1.

When tris(*N,N*-dimethyl-*o*-toluidyl)chromium [3], $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$, is treated with one or two molar equivalents of a metalla- β -diketone [4], the corresponding mixed-ligand complexes I—IV are formed. The complexes I and II complete a series of compounds since the tris(rhenaacetylacetonato) chromium complex has been prepared recently using $\text{Cr}[\text{N}(\text{i-Pr})_2]_3$ under similar reaction conditions [5].

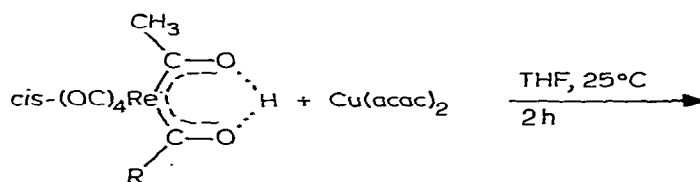
*For Part XX see ref. 1.



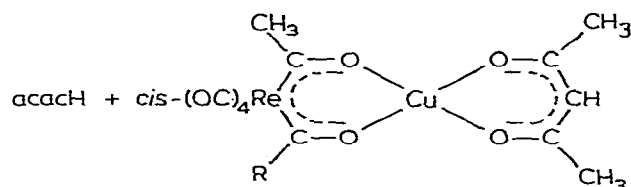
(R = Me, i-Pr, PhCH₂)



(I: R = Me, x = 1;
 II: R = Me, x = 2;
 III: R = i-Pr, x = 1;
 IV: R = PhCH₂, x = 1)



(R = CH₃, PhCH₂)



(V: R = CH₃;
 VI: R = PhCH₂)

SCHEME 1

Complex I crystallizes from ether solution as an analytically pure purple solid (anal. Found: C, 44.36; H, 4.40; N, 3.95; Cr, 7.12 C₂₆H₃₀N₂O₆CrRe calcd.: C, 44.31; H, 4.30; N, 3.98; Cr, 7.38%), and is isolated in a 10% yield. The solid is air stable for at least 4 h, and it melts at 100–103°C. The IR spectrum of I in C₆H₁₂ solution shows the expected four carbonyl stretching vibrations having the correct relative intensity pattern for a *cis*-(OC)₄Re moiety: 2090m, 1985s(sh), 1970vs, 1952 s cm⁻¹, and the rhenia chelate ring C—O stretch appears at 1510m cm⁻¹ [6,7]. There is no spectroscopic evidence indicating geometrical

isomerism. The magnetic moment, μ_{eff} , as determined by the Faraday method, is 3.85 BM which is consistent with three unpaired electrons located on the Cr atom. Upon standing in solution, complex I is converted into II and, presumably, $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ as revealed by IR.

The trinuclear complex (II) is isolated in 36% yield, and it crystallizes from hexane solution as analytically pure brown crystals (anal. Found: C, 31.74; H, 2.64; N, 1.40; Cr, 5.11. $\text{C}_{25}\text{H}_{24}\text{NO}_{12}\text{CrRe}_2$ calcd.: C, 31.44; H, 2.54; N, 1.47; Cr, 5.45%.) The solid melts at 114–115°C, and it is air stable for at least 4 h, also. The IR spectrum of II in hexane solution shows five terminal carbonyl stretching bands (2100m, 1995s(sh), 1987vs, 1978s(sh), 1959s cm^{-1}) and a rhenia chelate ring $\text{C}=\text{O}$ stretching band at 1510w cm^{-1} . The presence of more than four carbonyl bands is consistent with the very low molecular symmetry (C_1) of this complex. The magnetic moment, μ_{eff} , of 3.84 BM for complex II indicates a high spin d^3 -chromium atom.

The complexes III and IV are prepared using the same procedure. Although the observed color changes during the reactions and the final IR spectra of the reaction solutions indicated that the products are formed, the compounds could not be isolated as analytically pure solids. The unsymmetrical substitution on the metalla ligands may prevent facile crystallization of these molecules which probably exist as a mixture of isomers.

When a suspension of bis(acetylacetonato)copper, $\text{Cu}(\text{acac})_2$ in THF is treated with one molar equivalent of a metalla- β -diketone, the first examples of a mixed metalla- and non-metalla- β -diketonate complex (V and VI) are formed. Compound V also completes a chemical series since the bis(rheniacetylacetonato)-copper complex has already been prepared [2].

The complexes V and VI are isolated in ca. 15% yield, and they crystallize from pentane solution as analytically pure solids (V, anal. Found: C, 28.70; H, 2.68; Cu, 11.55. $\text{C}_{13}\text{H}_{13}\text{CuO}_8\text{Re}$ calcd.: C, 28.55; H, 2.39; Cu, 11.62%. VI, Found: C, 36.87; H, 2.89; Cu, 9.99. $\text{C}_{19}\text{H}_{17}\text{CuO}_8\text{Re}$ calcd.: C, 36.63; H, 2.75; Cu, 10.20%.) Complex V is a blue-green solid which decomposes sharply upon heating at 114–114.5°C, while VI is a blue-green and red dichroic solid which decomposes thermally at 88–89°C. Both complexes have a magnetic moment, μ_{eff} , of 1.91 BM which indicates one unpaired electron on the d^9 -Cu atom. The IR spectra of hexane solutions of V and VI show the four expected carbonyl bands and, also, a rhenia chelate ring $\text{C}=\text{O}$ stretch at ca. 1525 cm^{-1} . Two $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bands due to the acetylacetonate ligands are observed at 1535 and 1592 cm^{-1} , respectively.

The complexes I–VI are formed presumably via a ligand-exchange, elimination reaction due to the greater Brønsted acidity of the metalla- β -diketones relative to the acidity of acetylacetone or the tolyl-methyl carbon atom of *N,N*-dimethyl-*o*-toluidine. We believe that the successful exchange of these common types of bidentate, chelating ligands for metalla- β -diketonate ligands provides a general synthetic method for the preparation of other mixed-ligand complexes and thermally stable, paramagnetic organometallic complexes which contain two or more transition metal atoms. The extension of this preparative route and the spectroscopic study of the isolated paramagnetic complexes are being pursued.

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References

- 1 K.P. Darst and C.M. Lukehart, *J. Organometal. Chem.*, 171 (1979) 65.
- 2 C.M. Lukehart and G.P. Torrence, *Chem. Commun.*, (1978) 183.
- 3 L.E. Manzer, *J. Amer. Chem. Soc.*, 100 (1978) 8068.
- 4 C.M. Lukehart and J.V. Zeile, *J. Amer. Chem. Soc.*, 99 (1977) 4368.
- 5 C.M. Lukehart and G.P. Torrence, *Inorg. Chem.*, in press.
- 6 C.M. Lukehart, G.P. Torrence and J.V. Zeile, *Inorg. Chem.*, 15 (1976) 2393.
- 7 C.M. Lukehart and G.P. Torrence, *J. Chem. Soc. Dalton Trans.*, (1978) 93.