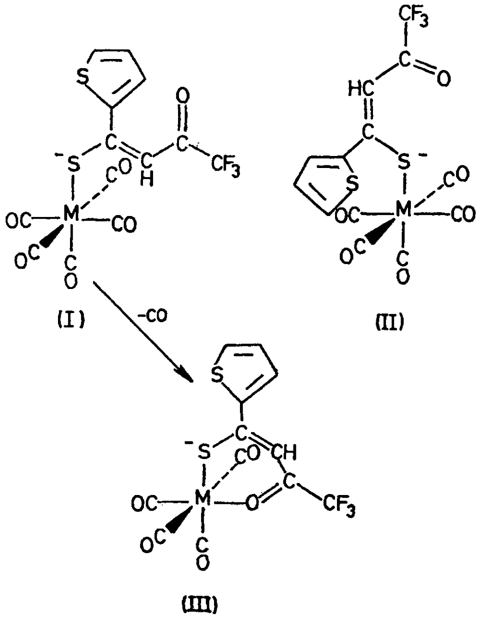
cis-trans-Isomerism in a Co-ordinated Monothio-β-diketone: *X*-Ray Structure of Tetraethylammonium Monothiothenoyltrifluoroacetonatopentacarbonyltungstate(o)

By MARY MCPARTLIN*† and GLEN B. ROBERTSON
(*Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia*)
and GEORGE H. BARNETT and MERVYN K. COOPER*
(*School of Chemistry, The University of Sydney, Sydney, 2006, Australia*)

Summary *X*-ray structure analysis has shown that the anion monothiothenoyltrifluoroacetonatopentacarbonyltungstate(o) (I) is the first metal complex in which a β-diketone type of ligand has been observed in its *trans*-isomeric form.

MONOTHIO-β-DIKETONES have been shown to form pentacarbonyls with the zerovalent metals of group VIA. They behave as monodentate sulphur donors with considerable localization of the π-electron density of the ligand skeleton.[1] In the title compound the *cis*-configuration of the co-ordinated ligand (II), hitherto observed in all metal complexes of β-diketones and monothio-β-diketones, appeared to lead to considerable steric interaction with the carbonyl groups. *X*-ray structure analysis shows that the ligand has avoided this by adopting the *trans*-isomeric form (I).



(I) (II) (III)

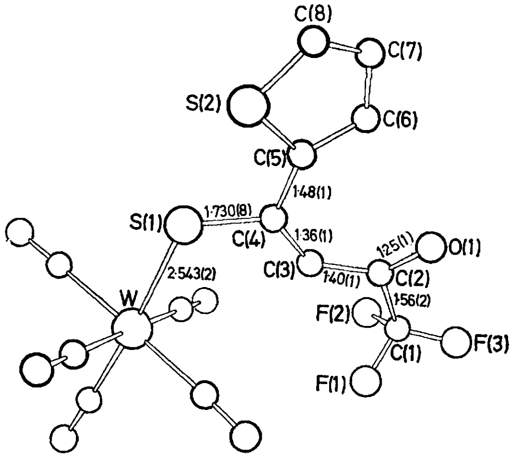


FIGURE. The structure of the complex anion $[W(CO)_5(C_8H_4OF_3S_2)]^-$ showing the principal bond lengths (e.s.d.'s in parentheses).

The only previous report of the *trans*-configuration of the co-ordinated ligand is for trimethylsiliconacetylacetonate which exists in solution as a mixture of the *cis*- and *trans*-isomers.[2] It is of interest that the formation of the tetra-

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† Present address: Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB.

carbonyl complex (III) by heating a solution of (I)[3] must involve isomerisation of the ligand from the *trans*- to the *cis*-form.

Orange-brown crystals of $C_{21}H_{24}NO_6F_3S_2W$ are orthorhombic, spacegroup $C\ 222_1$, $a = 8{\cdot}82$, $b = 18{\cdot}62$, $c = 31{\cdot}99$Å, $D_m = 1{\cdot}69$, $Z = 8$, $D_c = 1{\cdot}71$ g. cm^{-3}. Solution and refinement of the structure was based on 2559 unique reflections, $I/\Delta I \geqslant 3{\cdot}0$, recorded on a Picker FACS-1 fully automated four-circle diffractometer using graphite-crystal monochromated Cu-K_α radiation. Block-diagonal least-squares refinement (F isotropic, W,S,C,O anisotropic) using the absorption correction data ($\mu = 102{\cdot}5$ cm^{-1}) has given an R value of 0·044.

The structure of the complex anion and the relevant bond lengths are shown in the Figure. This clearly shows the unusual isomeric form of the ligand, with the co-ordinated sulphur atom S(1) *trans* to the carbonyl group C(2)–O(1) about the bond C(3)–C(4).

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