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Preliminary communication

Sulfur-donor ligand *ortho*-metalated complexes of ruthenium

HOWARD ALPER and ALBERT S.K. CHAN

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901 (U.S.A.)

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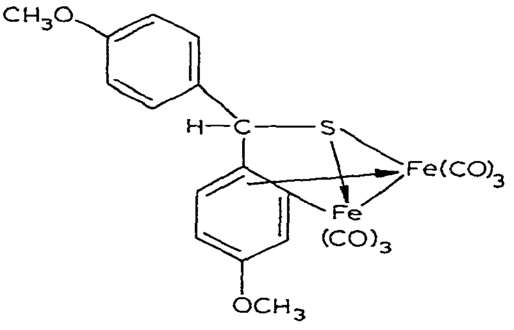
SUMMARY

Thiobenzophenones react with triruthenium dodecacarbonyl [$Ru_3(CO)_{12}$] in toluene to afford novel sulfur-donor ligand *ortho*-metalated complexes in high yield.

A recent paper[1] has described the first examples of sulfur-donor ligand *ortho*-metalated complexes (*e.g.* I), obtained by reaction of thiobenzophenones with diiron enneacarbonyl. We now wish to report that treatment of several thiones with $Ru_3(CO)_{12}$ results in the isolation of a novel type of *ortho*-metalated complex in high yield.

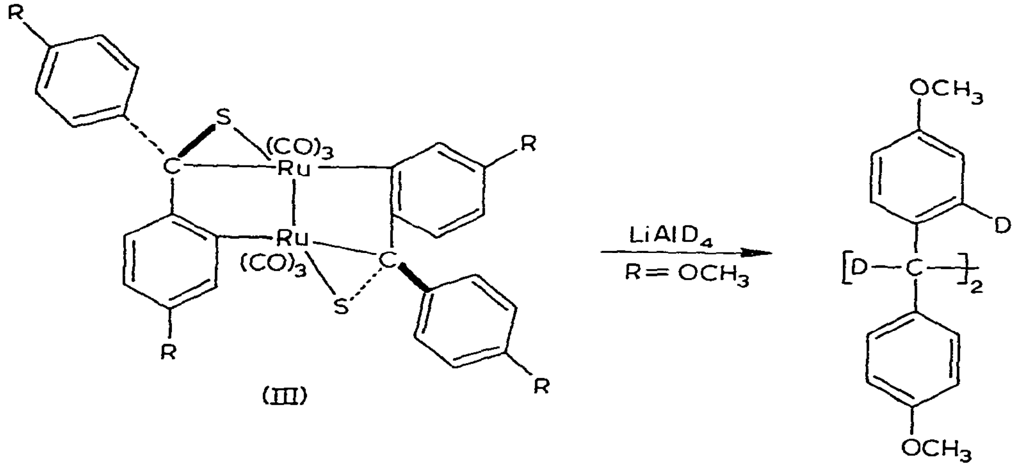


(I)

Reaction of 4,4′-dimethoxythiobenzophenone (II, R = OCH_3)[2] and $Ru_3(CO)_{12}$ in toluene at 70° [oil bath temperature] for 2.25 h gave, after chromatographic work-up [Florisil, 20% ether–petroleum ether (vol/vol) as eluant], complex III, R = OCH_3, m.p. 170° (dec.), in 90% yield [Found: C, 49.46; H, 3.21; S, 6.72. $C_{36}H_{26}O_{10}Ru_2S_2$ calcd.:

$$[p\text{-}RC_6H_4]_2CS \quad + \quad Ru_3(CO)_{12} \xrightarrow{C_6H_5CH_3}$$

$(II, R = OCH_3, CH_3)$



(III)

(IV)

C, 48.87; H, 2.98; S, 7.24%]. The structure proposed for this complex is based on analytical and spectral data as well as on reductive cleavage by lithium aluminum deuteride [$LiAlD_4$]. A vapor pressure osmometric molecular weight determination (889) was in excellent accord with the calculated value of 884 for III, R = OCH_3. Terminal metal carbonyl stretching bands were observed in the infrared (IR, CCl_4) at 2081 s, 2018 vs, 1995 s, and 1943 s cm^{-1} [KBr, ν(CO) 2078 s, 2010–1980 vs(br), and 1925 cm^{-1}]. The disappearance of the thiocarbonyl stretching absorption of II, R = OCH_3 [at 1217 cm^{-1}, KBr], upon complexation is noteworthy. The proton NMR spectrum ($CDCl_3$) of the complex displayed four singlets for the methoxy groups at δ 3.60, 3.64, 3.71 and 3.82. The aromatic protons appeared as a complex group of signals in the region of δ 6.38–7.70, those at the high field end of the range being characteristic of an *ortho*-metalated complex[1]. No bands were observed which could be assigned to a methine proton or to a hydride.

Exposure of III, R = OCH_3, to $LiAlD_4$ [in tetrahydrofuran] gave IV, R = OCH_3, whose structure is supported by analytical data, IR and NMR results, but most importantly, by a mass spectrum which indicated the presence of four deuterium atoms. Interestingly, complex III, R = OCH_3, undergoes carbon–sulfur bond cleavage while complexes of structural type I experience fission of the sulfur–iron bond on treatment with the metal hydride. This difference in behavior may be a consequence of the relative strengths of the S–Fe and S–Ru bonds with respect to the C–S bond. The cleavage experiment thus indicates the presence of two carbon–ruthenium σ bonds, one involving the benzylic carbon atom and the other involving an *ortho* carbon.

When II, R = CH_3 [3], was treated with $Ru_3(CO)_{12}$ in toluene at 70° for 7 h, the yellow complex III, R = CH_3 (m.p. 183° dec.), was isolated in 79% yield [Found: C, 53.05; H, 3.47; S, 7.85. $C_{36}H_{26}O_6Ru_2S_2$ calcd.: C, 52.67; H, 3.19; S, 7.81%]. The positions of the IR terminal metal carbonyl stretching bands for this complex [$CHCl_3$, ν(CO) 2085 s, 2020 vs(br), 1948 s cm^{-1}; KBr, 2080 ms, 2010–1985 vs(br), 1925 s cm^{-1}] were similar to those noted for III, R = OCH_3. Four distinct methyl signals were observed in the proton NMR at δ 2.12, 2.18, 2.31 and 2.38 ($CDCl_3$), and the aromatic protons again existed as a complex multiplet (δ 6.50–7.70).

Substituent effect studies are currently in progress.

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