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THIOKETONE-DITUNGSTEN DI- AND TRI-ANION REACTIONS

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Summary

The decacarbonylditungstate dianion, readily generated from tungsten hexacarbonyl and sodium amalgam, undergoes a facile reaction with thioketones to give (thioketone)pentacarbonyltungsten(0) complexes in good to excellent yields. The latter complexes, and the molybdenum analog, were formed by treatment of a thione with the chloride-bridged tungsten and molybdenum tricarbonylmetalates, $[M_2(CO)_6Cl_3]^{3-}$ (M = W, Mo).

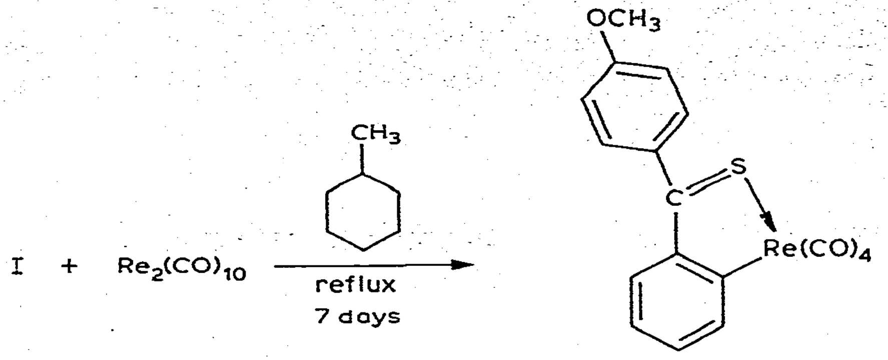
Neutral metal carbonyls react with thioketones to give a variety of novel organometallic complexes, several of which are important synthetic intermediates [1]. The chemistry of metal carbonyl monoanions with thioketones has also proved interesting, with initial thiophilic addition [2] occurring for manganese pentacarbonyl anion (e.g. I → II) [3] and for the cyclopentadienyl-iron, -molybdenum, and -tungsten carbonyl anions [4].

$$\underset{\text{(I)}}{(p\text{-}CH_3OC_6H_4)_2CS} + Mn(CO)_5^- \xrightarrow[CH_3I]{aq.\ CH_3OH} \underset{\text{(II)}}{[(p\text{-}CH_3OC_6H_4)_2CHSMn(CO)_4]_2}$$

Thus far, carbophilic addition has not been observed, perhaps because of the large effective bulk of the metal carbonyl anions used [5].

We now report a study of the reaction of thioketones with a carbonylmetal di- and tri-anion. A binuclear rather than a mononuclear dianion was used, since the anticipated thiophilic addition product in the former case would be a 1,4-dianion, for which repulsion between negative charges would be less than for a 1,3-dianion generated from a mononuclear dianion.

The dianion chosen for this investigation was the decacarbonylditungstate dianion, $W_2(CO)_{10}^{2-}$. This dianion is isoelectronic with dirhenium decacarbonyl, $Re_2(CO)_{10}$. The latter carbonyl undergoes sluggish thermal reaction with thiobenzophenones to give *ortho*-metalated complexes as the major product (e.g. III) [6]. Since the tungsten—tungsten bond in the dianion is weaker than the

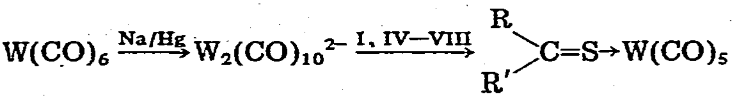


(III, 54 %)

rhenium—rhenium bond in $Re_2(CO)_{10}$ [7], a more facile reaction of $W_2(CO)_{10}^{2-}$ was expected with thioketones.

Results and discussion

The decacarbonylditungstate dianion was most conveniently generated by treatment of tungsten hexacarbonyl with sodium amalgam in 1,2-dimethoxyethane (DME) for 1 h at room temperature [8]. If desired, it could first be isolated as a bis(triphenylphosphine)iminium [9] or a tetraethylammonium salt [10]. Subsequent reaction of the dianion with a variety of aromatic and non-aromatic thioketones (I, IV—VIII) for a maximum of 30 min at room temperature



$$W(CO)_6 \xrightarrow{Na/Hg} W_2(CO)_{10}^{2-} \xrightarrow{I,\ IV—VIII} \begin{matrix} R \\ R' \end{matrix}\!\!>C{=}S{\rightarrow}W(CO)_5$$

(IX)

(IV = Ph_2CS; V = $(p\text{-}CH_3C_6H_4)_2CS$; VI = $PhCSC_6H_4OCH_3\text{-}p$; VII = adamantanethione; VIII = thiocamphor)

TABLE 1

YIELDS, MELTING POINTS, AND ANALYTICAL DATA FOR COMPOUND IX

IX		Color	Yield [a] (%)	M.p. (°C)	Anal. (Found (calcd.) (%))		
R	R'				C	H	S
$p\text{-}CH_3OC_6H_4$	$p\text{-}CH_3OC_6H_4$	Purple	66	91—92	41.63 (41.26)	2.56 (2.40)	5.93 (5.50)
Ph	Ph	Blue	85	55—57			
$p\text{-}CH_3C_6H_4$	$p\text{-}CH_3C_6H_4$	Purple	79	73—75	43.56 (43.66)	2.67 (2.56)	5.70 (5.83)
Ph	$p\text{-}CH_3OC_6H_4$	Purple	52	86—88	41.86 (41.33)	2.36 (2.19)	
$C_{10}H_{14}$		Orange	51	138—140 [c]			
$C_{10}H_{16}$		Orange	44	103—104	36.74 (36.62)	3.36 (3.25)	6.69 (6.50)

[a] Yield is based on $W(CO)_6$. [b] Lit. [11] m.p. 54—56°C. [c] Lit. [12] m.p. 138—139°C.

TABLE 2

PERTINENT SPECTRAL DATA FOR COMPOUND IX

IX		Infrared $\nu(CO)$ [a] (cm^{-1})	NMR δ (ppm) [b]
R	R'		
p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	2070m, 1985vw, 1952vs, 1932s	3.90 (s, 6H, OCH_3), 6.95 (d, 4H, J 9 Hz, protons *ortho* to methoxy bearing carbons), 7.58 (d, 4H, protons *meta* to methoxy bearing carbons)
Ph	Ph	2069m, 1975vw, 1952vs, 1936s	7.47 (m, 10H, aromatic)
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	2070m, 1953vs, 1933s	2.25 (s, 6H, CH_3), 6.88 (s, 8H, aromatic)
Ph	p-$CH_3OC_6H_4$	2069m, 1980vw, 1954vs, 1936s	3.97(s, 3H, OCH_3), 6.95 (d, 2H, J 9 Hz, protons *ortho* to methoxy bearing carbons), 7.56 (s, 5H, Ph), 7.75 (d, 2H, protons *meta* to methoxy bearing carbons)
$C_{10}H_{14}$		2072m, 1948vs, 1937s	
$C_{10}H_{16}$		2072m, 1986vw, 1948vs, 1938s	0.77 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.30—2.60 (m, 9H, other protons)

[a] Hexane as solvent: m, medium; vw = very weak; vs, very strong; s, strong. [b] $CDCl_3$ with tetramethylsilane (TMS) as internal standard.

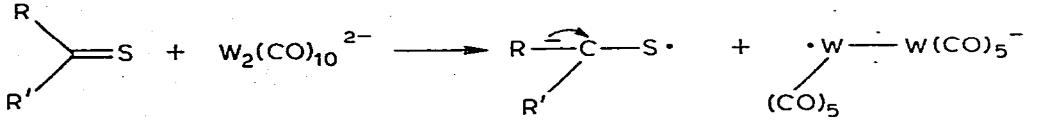
afforded (thioketone)pentacarbonyltungsten(0) complexes (IX), characterized on the basis of analytical and spectral data. The decacarbonylditungstate dianion is indeed much more reactive toward thioketones than $Re_2(CO)_{10}$.

The yields of pure thioketone complexes, as well as melting points and analytical data, are listed in Table 1. The yields of IX are, where comparable (e.g. for IX, R = R' = Ph), superior to those reported for complexes derived from reaction of $[(C_2H_5)_4N][W(CO)_5I]$ (prepared from $W(CO)_6$ and $(C_2H_5)_4NI$) with $AgBF_4$, ketone, and H_2S [11], or by irradiation of thioketones with tungsten hexacarbonyl [12].

The infrared spectra of IX displayed three principal metal carbonyl stretching vibrations, with a forbidden B_1 band detected in several instances. The proton magnetic resonance spectra are also in accord with the assigned structures (Table 2).

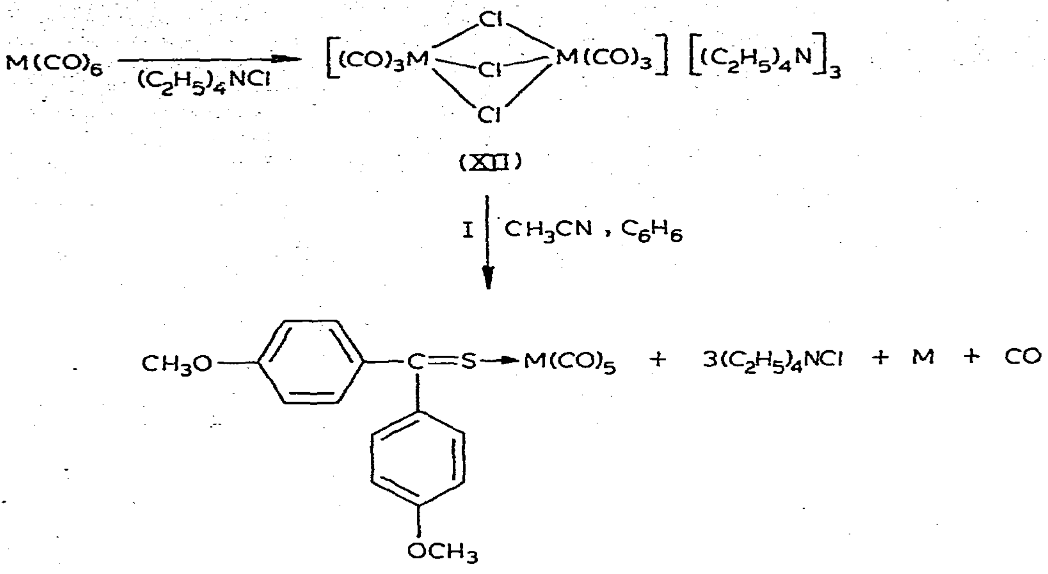
The reaction of thioketones with $W_2(CO)_{10}^{2-}$ may occur via initial electron transfer to give the organosulfur radical anion X and the ditungsten carbonyl radical anion XI.

Such an electron transfer process is likely for reactions of thiones with mononuclear metal carbonyl anions [3,4]. Several pathways are possible for the subsequent conversion of X and XI to IX.



(X) (XI)

Recently, Hohmann and tom Dieck [13] reported an efficient synthesis of chloride-bridged tungsten and molybdenum tricarbonylmetalates (XII, M = Mo, W), and some chemistry of the tungsten trianion has also been described [14]. A rapid disproportionation-ligand substitution reaction of I with XII, M = W



M=W(IX), Mo (XIII)

occurred in benzene containing acetonitrile to give the (thioketone)pentacarbonyltungsten(0) complex IX, R = R′ = p-$CH_3OC_6H_4$, in 25% yield (based on I). The stable molybdenum carbonyl complex XIII was similarly formed, in 26% yield, from XII, M = Mo and 4,4′-dimethoxythiobenzophenone.

Experimental

General

Melting points were determined using a Fisher—Johns apparatus, and are uncorrected. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, and by Butterworth Microanalytical Consulting Ltd., Teddington, Great Britain. Infrared spectra were recorded on a Unicam SP1100 spectrophotometer. Proton NMR spectra were obtained using a Varian T60 or HA100 spectrometer, with tetramethylsilane as the internal standard. An AEI 902S spectrometer was used for mass spectral determinations.

Tungsten hexacarbonyl (Pressure Chemical Co.) and 4,4′-dimethoxythiobenzophenone (I) (Aldrich Chemical Co.) were commercial products, and were used as received. Thiobenzophenone (IV) [15], 4,4′-dimethylthiobenzophenone (V) [15], 4-methoxythiobenzophenone (VI) [15], adamantanethione (VII) [16], and thiocamphor (VIII) [17] were synthesized according to literature methods. We are grateful to Climax Molybdenum Company for providing generous quantities of molybdenum hexacarbonyl.

Solvents were purifed by standard techniques. All reactions were run under a dry nitrogen or argon atmosphere.

General procedure for reaction of decacarbonylditungstate dianion with thioketones

A mixture of tungsten hexacarbonyl (0.88 g, 2.5 mmol) and sodium amalgam (0.5 g Na/5 ml Hg) in DME (50 ml) was stirred at room temperature for 1 h [8] Excess amalgam was removed, and the thioketone (I, IV—VIII, 5.0 mmol) was added to the $W_2(CO)_{10}^{2-}$ solution (in several instances, the $W_2(CO)_{10}^{2-}$ anion was first isolated as the bis(triphenylphosphine)iminium [9] or tetraethylammonium [10] salt). After stirring for 15—30 minutes, the reaction mixture was concentrated in vacuo and then chromatographed on Florisil (100—200 mesh; 15—35 cm long). Elution with hexane gave (thioketone) pentacarbonyltungsten(0) (IX). Complex IX could be purified further, if necessary, by crystallization from hexane (—78°C).

Reaction of 4,4'-dimethoxythiobenzophenone (I, R = R' = p-$CH_3OC_6H_4$) with XII (M = Mo)

The thioketone (1.03 g, 4.0 mmol) and $[(C_2H_5)_4N]_3[Mo_2Cl_3(CO)_6]$ [13] (1.70 g, 2.0 mmol) were dissolved in a mixture of acetonitrile (5 ml) and benzene (50 ml), and the reaction mixture was then stirred at room temperature for 2 h. The solvents were removed by flash evaporation and the residue was chromatographed on silica gel using hexane. Elution with 10% benzene/hexane gave 0.52 g (26% yield based on thioketone) of the purple complex XIII, m.p. 81—82°C.

Anal.: Found: C, 48.61; H, 2.77; S, 6.82. $C_{20}H_{14}MoO_7S$ calcd.: C, 48.59; H, 2.85; S, 6.49%. Ir(C_6H_{14}), ν(CO): 2070m, 1960vs, 1935s cm^{-1}. PMR ($CDCl_3$): δ (ppm) 3.92 (s, methoxy groups). 6.97 (d, J 9 Hz, protons *ortho* to the methoxy bearing carbons), 7.60 (d, protons *meta* to the methoxy bearing carbons). Mass spectrum (*m/e*) 494 [M^+], 466 $[M - CO]^+$, 410 $[M - 3CO]^+$, 382 $[M - 4CO]^+$, 354 $[M - 5CO]^+$, 258 [4,4'-dimethoxythiobenzophenone].

Reaction of 4,4'-Dimethoxythiobenzophenone (I, R = R' = p-$CH_3OC_6H_4$) with XII (M = W)

Reaction of 4,4'-dimethoxythiobenzophenone (1.03 g, 4.0 mmol) and $[(C_2H_5)_4N]_3[W_2Cl_6(CO)_6]$ [13] (2.06 g, 2.0 mmol) as described for XII, M = Mo gave 0.59 g (25%) of IX.

Acknowledgement

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