The synthesis of η^2-thioketenyl complexes of molybdenum and tungsten

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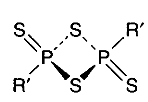
The complexes [M(η^2-OCCR)(CO)L(Tp)] [M = Mo, W; L = $P(OMe)_3$, PMe_2Ph, PPh_3; R = C_6H_4Me-4; Tp = hydrotris(pyrazol-1-yl)borate] are obtained from [M(≡CR)$(CO)_2$(Tp)] and L under photolysis and these react with Lawesson's reagent $(S_2PC_6H_4OMe\text{-}4)_2$ to provide thioketenyl complexes [M(η^2-SCCR)(CO)L(Tp)] one example of which (M = W, L = PMe_2Ph) is also obtained from the reaction of [W(η^2-ClCCR)Cl(CO)(Tp)] with NaSH in the presence of PMe_2Ph.

Lawesson's reagent **1** has enjoyed considerable application as an oxygen/sulfur exchange reagent in organic synthesis.[1] Although some reports have appeared concerning the coordination chemistry of **1**, these have exclusively involved ligands derived from the fragmentation of **1**, *e.g.* **2**–**4**.[2,3]

Compared to simple metal carbonyls L_nMCO, analogous chalcogenocarbonyl ligands L_nMCE (E = S, Se, Te) show a considerably enhanced reactivity towards electrophilic and nucleophilic attack and a substantial propensity for migratory insertion and ligand-coupling processes.[4] Kreißl and coworkers have extensively illustrated the enormous synthetic potential of ketenyl complexes[5] and we were therefore intrigued by the added dimension of reactivity offered by thioketenyls, given that they have on occasion been implicated as plausible reaction intermediates.[6] Towards this end we were encouraged by the very recent isolation of a thioketenyl complex of tungsten [W(η^2-SCCPh)I(CO)(CNR)$(PMe_3)_2$] (R = Bu^t, $C_6H_3Me_2$-2,6), presumed to result from the coupling of thiocarbonyl and alkylidyne ligands in the putative intermediate complex [W(≡CPh)I(CO)(CS)$(PMe_3)_2$].[7] We report herein: (*i*) the photochemical synthesis of a range of η^2-ketenyl complexes of molybdenum and tungsten; (*ii*) the first application of **1** as a sulfur/oxygen exchange reagent in organotransition-metal chemistry; (*iii*) the apparently general conversion of ketenyl complexes to the corresponding thioketenyl complex by treatment with **1**; and (*iv*) the conversion of a chloroalkyne to a thioketenyl ligand.

We have recently reported the synthesis of [W(η^2-OCCR)(CO)(PPh_3)(Tp)] **5a** [hereafter R = C_6H_4Me-4; Tp = hydrotris(pyrazol-1-yl)borate] *via* a thermal reaction of photochemically generated all-*trans*-[W(≡CR)Br$(CO)_2(PPh_3)_2$] with KTp.[8] The complex [Mo(η^2-OCCR)(CO)(PPh_3)(Tp)] **5b** is not available by the same route, the otherwise inaccessible alkylidyne complex [Mo(≡CR)(CO)(PPh_3)(Tp)] being the exclusive product. Furthermore, the complexes [M(≡CR)$(CO)_2$(Tp)] do not react thermally with PPh_3. It transpires, however that the complexes [M(η^2-OCCR)(CO)L(Tp)] **5** [M = Mo, W; L = PPh_3, $P(OMe)_3$, PMe_2Ph] may be prepared *via* photolysis of [M(≡CR)$(CO)_2$(Tp)] in the presence of phosphines (L). These compounds thermally revert in solution to either [M(≡CR)$(CO)_2$(Tp)] or [M(≡CR)(CO)L(Tp)] depending on L, however they may be isolated at low temperature and stored indefinitely in the solid state (Scheme 1).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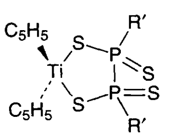
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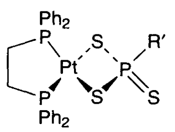
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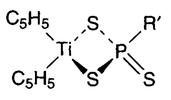
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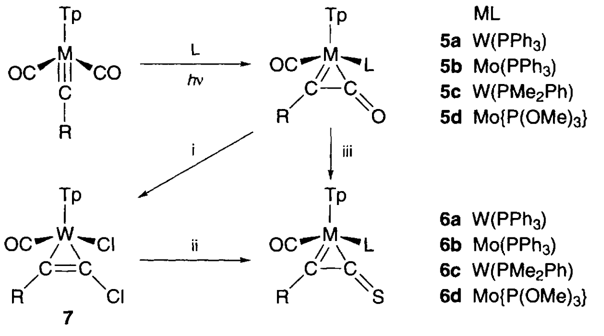
R′ = C_6H_4OMe-4

Treating [M(η^2-OCCR)(CO)L(Tp)] **5** with 1 equiv. of **1** in tetrahydrofuran resulted in the formation of the desired thioketenyl complexes [M(η^2-SCCR)(CO)L(Tp)] **6** in high yield as the only isolable organometallic products. The reactions proceed cleanly in all cases and are essentially complete within seconds. In other solvents investigated (diethyl ether, toluene) the reaction failed to provide tractable products. The green complexes were found to be moderately air-stable in all cases, both in the solid state and in chloroform solution. All spectroscopic and analytical data were consistent with the formulations and data for one illustrative example, **6c**, are presented in Table 1 in addition to those for the corresponding



Scheme 1 *Reagents*: i, Ph_3PCl_2; ii, NaSH, PMe_2Ph; iii, $(S_2PC_6H_4OMe)_2$; M = W, Mo; L = PPh_3, $P(OMe)_3$, PMe_2Ph; R = C_6H_4Me-4; Tp = κ^3-HB$(pz)_3$

Table 1 Selected spectroscopic data for the complexes [W(η^2-ECCR)-(CO(PMe_2Ph)(Tp)]; E = O **5c**, S **6c**

	5c	**6c**
Colour	purple	green
IR (Nujol/cm^{-1})		
ν(WCO)	1885	1905
ν(CE)	1675	939
NMR ($CDCl_3$,25 °C)		
$^{31}P\{^1H\}$ δ(WP)[*J*(WP)/Hz]	−0.90[339]	−4.19[332]
$^{13}C\{^1H\}$ δ(WRC*C*E)[a]	207.7	230.8
δ(WR*C*CE)[a]	228.8	231.2
δ(WCO)[*J*(PC)/Hz]	218.3[3.6]	233.7[3.6]
FAB-MS (noba matrix) *m/z* (abundance %)		
$[M]^+$	695(20)	710(90)
$[M-CO]^+$	666(11)	682(43)
$[M-2CO]^+$	637(10)	[b]
$[MH-PMe_2Ph]^+$	556(24)	[b]
$[M-L-CO]^+$	528(17)	544(100)
$[M-L-2CO]^+$	500(20)	[b]

NMR data relative to $SiMe_4$ (^1H and ^{13}C) or H_3PO_4 (^{31}P). [a] Unequivocal assignment not possible. [b] Not observed.

ketenyl complex, **5c**, for comparison. The following data are particularly noteworthy. The thioketenyl ligands give rise to an IR absorption in the range 930–945 cm^{-1} which may be assigned primarily to ν(C=S). The ^{13}C NMR chemical shifts of the thiocarbonyl carbons fall in a narrow range δ 230–233, which is within the more dispersed range for corresponding ketenyl resonances. This is perhaps surprising given that terminal thiocarbonyl ligands are typically shifted downfield by up to 100 ppm compared with carbonyl resonances. Whilst peaks attributable to $[M - CO]^+$ predominate in the FAB mass spectrum of the ketenyl complexes, $[M - CS]^+$ peaks are essentially absent for the thioketenyl analogues.

An alternative, though less general, route to thioketenyl complexes has also been developed, utilising the nucleofugicity of the chloro substituent of a recently reported chloroalkyne complex $[W(\eta^2\text{-ClCCR})Cl(CO)(Tp)]$ **7**.[8] It was initially envisaged that reaction of **7** with sodium sulfide would provide the coordinatively unsaturated thioketenyl complex '$[W(\eta^2\text{-SCCR})(CO)(Tp)]$' which might be expected to decouple the CS and CR components of the thioketenyl ligand to provide $[W(\equiv CR)(CS)(CO)(Tp)]$. However if such species form they have not been amenable to isolation. Nevertheless, if the reaction is carried out in the presence of PMe_2Ph, the thioketenyl complex **6c** is obtained in good yield.

In addition to illustrating two new routes to thioketenyl complexes, the results described herein indicate that the thioketenyl ligand is not readily prone to decoupling, and demonstrate the synthetic utility of haloalkynes as synthons for C_2 ligands. The use of Lawesson's reagent for the preparation of organosulfur ligands has been demonstrated and offers considerable synthetic potential, which we are currently investigating.

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Footnote

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