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Preliminary communication

π-ALLYLDICARBONYLCHROMIUM(II) COMPLEXES

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Summary

The reaction of $[M(CO)_3\,\text{bidentate}X]^-$ anions (M = Group VIA element) with allyl chloride under mild conditions yields π-allyl complexes of the type $XM(CO)_2(\pi\text{-allyl})$bidentate and provides a route to the previously unknown chromium compounds and a facile synthesis of the corresponding molybdenum and tungsten complexes.

While investigating some π-allyl compounds of the type $XM(\pi\text{-allyl})(CO)_2$ bidentate, where M = Group VIA element, we have developed a synthetic method which can be used to prepare π-allyldicarbonyl complexes of all three elements.

Previous synthetic routes, which are restricted to molybdenum and tungsten, are summarised below:

$$\begin{tikzcd} \text{(a) } Et_4N[M(CO)_5Y] + \text{allyl-X} \arrow[r] & Et_4N[M_2(CO)_4(\pi\text{-allyl})_2X_3) \arrow[d, "L_2"] \\ & XM(CO)_2(\pi\text{-allyl})L_2 \end{tikzcd}$$

where X = Cl, M = Mo or W (ref. 1)

$$\begin{tikzcd} \text{(b) } W(CO)_6 + \text{allyl-X} \arrow[r, "h\nu"] & XW(CO)_4(\pi\text{-allyl}) \arrow[d, "L_2"] \\ & XW(CO)_2(\pi\text{-allyl})L_2 \end{tikzcd}$$

where X = Br, I (ref. 2)

$$\begin{tikzcd} \text{(c) } \mathrm{Mo(CO)_4L_2} + \text{allyl-X} \arrow[r] & \mathrm{XM(CO)_2}(\pi\text{-allyl})\mathrm{L_2} \arrow[d, "Y^-"] \\ (\mathrm{M(CO)_3L_2L'}) & \mathrm{YM(CO)_2}(\pi\text{-allyl})\mathrm{L_2} + X^- \end{tikzcd}$$

where X = Cl, Br, I or NCS
M = Mo or W
Y = SC_6F_5, NCS (refs. 3 and 4)

Methods (a) and (b) are limited by the availability of the initial π-allyl—metal complexes and so cannot be used for chromium. Method (c) is the most general but involves reaction conditions under which the corresponding chromium complexes decompose. Furthermore, neutral metal carbonyl derivatives of molybdenum and tungsten are not oxidised by many allyl compounds under the conditions used for the halide reactions, while anion exchange is of limited use only.

We find that the anionic species $[M(CO)_3\,\text{bidentate}X]^-$ react readily with allyl chloride at or below room temperature to yield $XM(CO)_2$ (π-allyl)-bidentate complexes for chromium, molybdenum and tungsten. The chromium complexes can be isolated by this method because of the very mild conditions of the reaction, while a range of π-allyl—molybdenum and —tungsten derivatives can be synthesised directly from a single allyl compound. The $[M(CO)_3\text{-}\text{bidentate}X]^-$ anions may be prepared from $C_7H_8M(CO)_3$ by Behren's method [5], or more conveniently formed in situ bv the reaction of Na^+ or R_4As^+ salts with $M(CO)_4$ bidentate in acetonitrile. In a typical experiment 0.39 g $Cr(CO)_4$ dipyridyl was refluxed for three hours with 0.76 g NaI dissolved in 20 ml acetonitrile under an atmosphere of nitrogen. The solution was cooled to 0° C, filtered and added dropwise to 1 ml allyl chloride in 15 ml methanol maintained at —10° C. The red-brown product was filtered off, washed with water to remove sodium salts and dried in vacuo. Yield 73%. The corresponding chromium chloride and bromide products did not precipitate but were isolated by washing the residue obtained by evaporation of the filtrate with water. The chloride was always contaminated with traces of $Cr(CO)_4$ dipyridyl. An analogous procedure carried out at room temperature was used to prepare molybdenum and tungsten complexes. All three series of complexes exhibited two bands of approximately equal intensity in the C—O stretching region of their infrared spectra, as expected for *cis*-dicarbonyl complexes (Table 1).

The new chromium compounds are essentially diamagnetic, although slight paramagnetism was detected in some samples (e.g. $ICr(CO)_2$ (π-allyl)-dipyridyl, $\chi_M \sim 250 \times 10^{-6}$ cm^3 mol^{-1}). This is probably caused by traces of chromium(III) impurities which arise through a disproportionation reaction of chromium(II). This reaction is very slow in the solid state but is rapid in solution and results in the formation of $Cr(CO)_4$ dipyridyl as the reduced product. In view of this, no reliable NMR data has been obtained so far, so that the bonding mode of the allyl group has been inferred by a comparison of the solid-state infrared spectra of the chromium complexes with those of the π- and σ-bonded allyl complexes of molybdenum, tungsten, manganese and palladium [6—10]. Although many of the allyl bonds are obscured by dipyridyl absorptions, those which are observed are typical

TABLE 1

ANALYTICAL AND PARTIAL INFRARED DATA FOR Cr^{II} COMPLEXES

Compound	ν(C—O) ^{a} (cm^{-1})	ν(C—N) ^{a} (cm^{-1})	Analytical data found (calcd.) (%)		
			C	H	N
ClCr(CO)$_2$ (π-allyl)(dipy)	1932, 1848		51.9	4.0	8.47
			(52.8)	(3.8)	(8.21)
BrCr(CO)$_2$ (π-allyl)(dipy)	1930, 1852		45.5	3.5	6.97
			(46.8)	(3.4)	(7.27)
ICr(CO)$_2$ (π-allyl)(dipy)	1925, 1853		41.2	3.2	6.65
			(41.6)	(3.1)	(6.48)
SCNCr(CO)$_2$ (π-allyl)(dipy)	1947, 1865	2100	52.5	3.9	11.3
			(52.9)	(3.6)	(11.6)

^{a} Nujol mull.

of a π-bonded allyl group, indicating that these new chromium complexes are formally seven coordinate, and analogs of the well-known molybdenum(II) and tungsten(II) complexes.

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