Preliminary communication

Transition metal carbene complexes
## LXIV[*]. Vinylmethoxycarbene–pentacarbonylchromium(0)

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The nature of the bonding associated with the carbene carbon atom in transition metal carbene complexes (I) still seems to be a challenge, although it is now generally accepted that stabilisation of the electrophilic carbene carbon is achieved in part by $d_\pi-p_\pi$ backbonding from the transition metal but in the main via electron donation by the basic atom in X and in some cases also in Y. Further, it is observed that nitrogen is more efficient in this respect than oxygen, sulphur or selenium. Recently ^{13}C NMR spectroscopy has indicated that in these compounds the carbene carbon atom has a similar chemical shift to those observed for carbonium ions and hence may carry an appreciable positive charge[2].
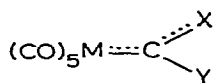
(I)
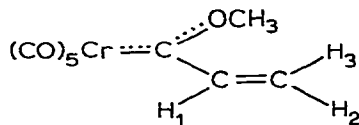
(II)

M = Cr, Mo, W.
X = a group containing a basic atom (O^-, OR', SR', SeR', NR_2', PR_2')
Y = alkyl, aryl, heterocyclic group or a group containing a basic atom.

The title compound (II) has been prepared in order to gain further insight into the problem. This compound is of interest since if the carbene carbon atom does carry a significant amount of positive charge then when Y = vinyl, the carbon chain is an incipient 1,1′-disubstituted allyl cation. The chemical and spectroscopic properties of the compound should provide further information to test the bonding model. The purported preparation and partial characterisation of the compound have appeared in the literature[3,4].

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EXPERIMENTAL

All preparations and experiments were carried out under an atmosphere of purified nitrogen. Solvents were deoxygenated and sodium dried.

The stoichiometric amount of a freshly prepared ethereal solution of vinyllithium[5] diluted to 100 ml with ether was added to a rapidly stirred solution of hexacarbonyl-chromium(0), 2.2 g (10 mmol) in ether over 2 h. After further stirring at room temperature for 1 h the solvent was removed under reduced pressure (oil pump). The residue was dissolved in the minimum amount of CH_2Cl_2 and pentane (100 ml) added. A slight excess of finely divided trimethyloxonium tetrafluoroborate was added and dispersed in the mixture by rapid stirring. Deoxygenated water (5 ml) was added and the mixture stirred for 1 min. The organic layer was quickly dried and filtered by decanting it through a layer of Na_2SO_4 supported on a G3 frit. The solvent was removed at 0° under reduced pressure to give a dark red residue. This was purified by column chromatography (Kieselgel, pentane) using a water cooled column (1.50 m, dia. 1.5 cm). Concentration of the red fraction and cooling at −78° produced dark red crystals. m.p. 15°. [Found C, 41.15; H, 2.43; O, 36.10; Cr, 20.31. Mol. wt. 262 (mass spec.). $C_9H_6O_6Cr$ calcd.: C, 41.22; H, 2.31; O, 36.63; Cr, 19.84%. Mol. wt. 262.16]. IR (cm^{-1}, n-hexane) CO region: 2062m, 1963s and 1946vs. The ν(C=C) could not be observed. Yields varied between 20 and 35% (*vide infra*).

The compound sublimes at 10° (oil pump) and is soluble in organic solvents. These solutions are relatively stable to oxygen but fairly sensitive to moisture, hence the variable yields obtained. The crystals melt to a mobile liquid which soon solidifies, without colour change, into a polymeric glass. This is unaffected by water and oxygen and insoluble in organic solvents. It begins to decompose at 70° and $Cr(CO)_6$ sublimes to the cooler parts of the sealed melting point tube.

RESULTS AND DISCUSSION

Mass spectrum

The fragmentation pattern observed is typical of a transition metal carbonyl carbene complex. The chromium-containing peaks are given in Table 1.

NMR

^{1}H (CDCl$_3$, internal TMS). Assignment of the twelve line ABX system was made by comparison with similar organic systems. The appropriate τ values (ppm) and coupling constants (Hz) are: τ 2.41 (H$_1$, dd.), 4.45 (H$_3$, dd.), 4.93 (H$_2$, dd.), 5.15 (OCH$_3$, s); J(H$_1$–H$_2$) 10.5, J(H$_1$–H$_3$) 16.5, J(H$_2$–H$_3$) 1.4.

^{13}C (CDCl$_3$, internal TMS). The proton decoupled spectrum showed the expected six absorptions downfield from TMS: δ(carb) 323.22, δ(CO-*trans*) 223.97, δ(CO-*cis*) 216.41, δ(CH) 148.77, δ(CH$_2$) 114.90 and δ(OCH$_3$) 66.78. Assignments were made by comparison with similar systems and from the observation that in the proton undecoupled spectrum the signal at 115.0 was a triplet.

TABLE 1

MASS PEAKS OF $(CO)_5CrL$ $(L = -C(Y)X, Y = (CH=CH_2), X = OCH_3)$

Ion	m/e	Rel. Int.	Ion	m/e	Rel. Int.
$(CO)_5CrL^+$	262	24	$(CO)C-C{\stackrel{O^+}{\diagdown}}_{Y}$	135	2
$(CO)_4CrL^+$	234	3	CrL^+	122	100
$(CO)_3CrL^+$	206	3	$Cr-C{\stackrel{O^+}{\diagdown}}_{Y}$	107	17
$(CO)_2CrL^+$	178	19	$Cr-C{\stackrel{H^+}{\diagdown}}_{Y}$	92^a	7
$(CO)CrL^+$	150	19	$Cr-Y^+$	79	40
			Cr^+	52	95

a This species is attributed to the loss of formaldehyde from CrL^+ and is usually too unstable to be observed in the mass spectrum of transition metal carbonyl carbene complexes. Its assignment is supported by the presence of the appropriate metastable peak. The involatile polymeric glass decomposed in the spectrometer to give the spectrum of $Cr(CO)_6$.

The following observations indicate the extent to which the vinyl group participates in the stabilisation of the carbene carbon atom. The upfield shift of ≈ 39 ppm for δ(carb) from the value for the corresponding methyl derivative is close to that observed when Y is a heterocyclic group[2b] and is consistent with increased electron density at the carbene carbon atom. The appearance of $Cr-CH(CH=CH_2)$ in the mass spectrum is also attributed to the stabilising effect of the vinyl group.

Comparison of the ^1H and ^{13}C chemical shifts in the carbene complex with those for the corresponding atoms in the parent hydrocarbon propene are given in Table 2[6,7].

TABLE 2

COMPARISON OF THE ^1H AND ^{13}C CHEMICAL SHIFTS (τ and δ_C in ppm) FOR PROPENE AND VINYLMETHOXYCARBENE–PENTACARBONYLCHROMIUM

	^1H			^{13}C	
	H_1	H_2	H_3	CH	CH_2
Propene	4.27^a	5.12^a	5.04^a	133.1^b	115.0^b
Carbene complex	2.41	4.93	4.45	148.77	114.90

a In dilute CCl_4 solution. b Solvent unspecified.

It is seen that in the carbene complex the H_1 proton is considerably deshielded whereas H_2 and H_3 are moved downfield to a lesser extent. Similarly for the ^{13}C chemical shifts $\delta(CH)$ undergoes a significant downfield shift whilst $\delta(CH_2)$ apparently remains unchanged. It would appear therefore that the vinyl group stabilises the carbon carbene atom via a sigma inductive mechanism.

These results do not agree with those reported by Connor and Jones for this compound[3,4]. A possible explanation is their use of a solution of trimethyloxonium tetrafluoroborate in methylcyanide as the alkylating agent. Such systems are known to form stable "nitrilium" salts $[RC{\equiv}NR']BF_4$ which have potentially different modes of reaction to the free oxonium salts[8]. The use of these reagents in transition metal carbonyl carbene chemistry is under investigation.

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