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PHOTOCHEMICAL REACTIONS OF ALLYL AND CROTYL HALIDES WITH CYCLOPENTADIENYL-CHROMIUM, -MOLYBDENUM AND -TUNGSTEN COMPLEXES

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Summary

$[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ on photolysis with allyl or crotyl halides C_5H_4RX gives Mo^{IV} complexes $[MoX_2(CO)(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5H_5)]$ (R = H, X = Cl, Br, I; R = Me, X = Cl, Br). $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ under similar conditions gives trihalides $[WX_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (X = Cl, Br) on reaction with C_3H_5Cl and C_3H_5Br while $[WCl(CO)_3(\eta^5\text{-}C_5H_4SiMe_3)]$ and $[CrI(CO)_3(\eta^5\text{-}C_5H_5)]$ react with allyl chloride to give $[WCl_3(CO)_2(\eta^5\text{-}C_5H_4SiMe_3)]$ and $[CrCl_2(\eta^5\text{-}C_5H_5)]$ respectively.

Introduction

We previously presented evidence that cyclisation of alkynes in complexes $[MCl(RC{\equiv}CR)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) to give cyclobutadiene [1] and cyclopentadiene [2] derivatives proceeds via metallocyclic intermediates. This requires that the metal undergoes the familiar oxidative addition, reductive elimination processes with in this case an intermediate M^{IV} organometallic species. Relatively few molybdenum- and tungsten(IV) organometallics are known [3,4], the most relevant examples in this case being halogeno derivatives $[MX_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, W; X = Cl, Br, I), which were prepared by halogen [4d] or organohalide [5] oxidation of divalent complexes $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$. Halogen oxidation of zero valent hexacarbonyls $[M(CO)_6]$ (M = Mo, W) readily gives $[MX_2(CO)_4]_2$ [6] while the analogous reaction of $[W(CO)_6]$ with allyl halides gives $[WX(CO)_4(\eta^3\text{-}C_3H_5)]$ (X = Cl, Br, I) [7]. This prompted us to study the reactions of $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) with allyl halides with a view to isolating higher oxidation state molybdenum and tungsten organometallics. The recent report that ruthenium(IV) allyls $[RuX_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5R_5)]$ (X = Cl, Br or I; R = H or Me) can be obtained from the oxidative addition of allyl halides to ruthenium(II) complexes

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$[RuX(CO)_2(\eta^5\text{-}C_5R_5)]$ (X = Cl, Br, R = H or Me) [8] now prompts us to report the results of studies carried out to date.

Results and discussion

Photolysis of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ as a solution in neat allyl halide C_3H_5X (X = Cl, Br or I) gave deep red crystalline complexes $[MoX_2(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ (I) while the bromide Ib was similarly obtained on reaction of $[MoBr(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl-bromide. The iodide Ic obtained was impure, and because of its relatively low solubility in suitable organic solvents it could not be purified adequately for analytical purposes. The crotyl complexes $[MoX_2(CO)(\eta^3\text{-}C_3H_4Me)(\eta^5\text{-}C_5H_5)]$ (II) were similarly prepared on photolysis of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ in neat crotyl halides, C_3H_4MeX (X = Cl, Br) but it was subsequently found that reactions carried out using diethyl ether as a solvent gave better results. In contrast $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ reacts with C_3H_5X (X = Cl or Br) on photolysis to give trihalides $[WX_3(CO)_2(\eta^5\text{-}C_5H_5)]$ (III) (X = Cl or Br), prepared previously by alkyl halide [5] or halogen [4a] oxidation of $[WX(CO)_3(\eta^5\text{-}C_5H_5)]$. Attempts to prepare allyl tungsten derivatives by modifying the C_5H_5 were unsuccessful, since C_3H_5Cl and $[WCl(CO)_3(\eta^5\text{-}C_5H_4SiMe_3)]$ similarly gave $[WCl_3(CO)_2(\eta^5\text{-}C_5H_4SiMe_3)]$ (IV). In contrast the chromium complex $[CrI(CO)_3(\eta^5\text{-}C_5H_5)]$ underwent complete decarbonylation on photolysis in allyl chloride to give the previously characterised [9] dichloride $[CrCl_2(\eta^5\text{-}C_5H_5)]$ (V) as deep blue crystals. In general, apart from Ic analytically and spectroscopically pure crystalline products were usually isolated from these reactions and further purification was found to be unnecessary. However in some instances, when rigorous deoxygenation of the allyl halide was not carried out, or when the photolysis was allowed to proceed for longer periods, some decomposition was observed, particularly in reactions of the tungsten derivatives. The previously characterised complexes III and V were identified either by comparison spectroscopically with authentic samples or where necessary by full spectroscopic and analytical characterisation. The new complexes I, II and IV were fully characterised.

As expected the allyl and crotyl complexes I and II exhibit a single $\nu(CO)$ mode in the IR spectrum and the mass spectra show prominent ions $[M-CO]^+$, $[M-(CO+C_3H_4R)]^+$ and $[M-(CO+C_3H_4RX)]^+$. The $\nu(CO)$ mode in each case lies above 2000 cm^{-1}, reflecting the high oxidation state of the metal and consequent reduction in $M-CO$ π-back donation. Few structural studies of Mo^{IV} cyclopentadienyl complexes have been reported but in $[MoI_3(CO)_2(\eta^5\text{-}C_5H_4Me)$ [10] and $[\overline{MoC(CF_3)=C(CF_3)\text{-}C(CF_3)=C}(CF_3)(CO)_2(\eta^5\text{-}C_5H_5)Co(CO)_2]$ [11] the molybdenum atom adopts the square-based piano stool geometry found in Mo^{II} cyclopentadienyl complexes but with an extra ligand capping the square base. Such a structure might be expected for complexes I and II but with possible distortions due to the presence of the allyl group, and consequently a single crystal X-ray diffraction study of $[MoCl_2(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ was carried out [12]. However the crystals were found to be severely disordered and about the only safe conclusion from the crystallographic work is that the disordered structure cannot be shown to be inconsistent with the proposed formulation. Firgures 1a and 1b show a choice of disordered atoms giving an internally self-consistent geometry which can be described as a square piano stool thus implying a relationship to the structures already

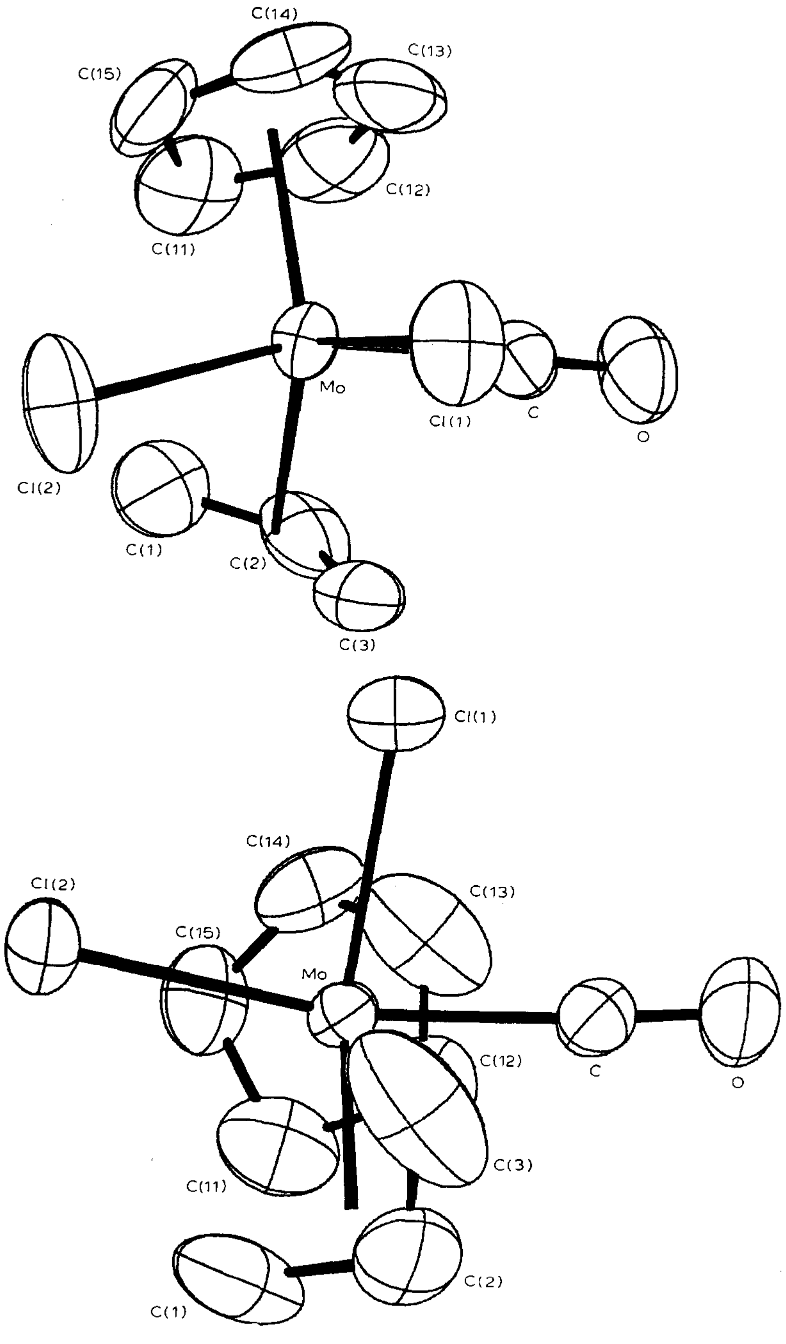
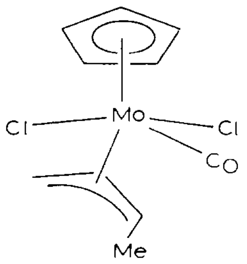


Fig. 1a and b. Two views of $[\mathrm{MoCl_2(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)}]$. The crystal is disordered and the observed electron density is consistent with superposition of two molecules related by mirror reflection in the MoCl(1) CO plane.

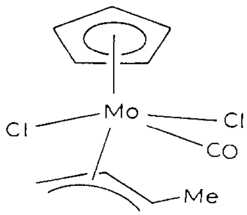
described. A closer analogy can be drawn with the η^3-cyclopropenyl complex $[WCl_2(PMe_3)(\eta^3\text{-}C_3Ph_3)(\eta^5\text{-}C_5H_5)]$ the structure of which approaches the idealised four legged piano stool if the cyclopropenyl ligand is considered to occupy a single coordination site [13].

Although this geometry could conceivably give rise to several isomeric forms the ^1H NMR spectra of allyl derivatives I (a, b and c) indicate that in solution only one species is present. The five distinct proton signals in the region δ 3–6 ppm are clearly in accord with the asymmetric environment adopted by the allyl ligand in the solid state and a similar structure seems probable. In contrast two forms of the crotyl complexes are present in solution, ratio 2/1 (IIa) and 10/3 (IIb). Since only one allyl form is present we assume that isomerism in the crotyl derivatives results from the presence of two possible methyl group positions either in *syn* and *anti* forms e.g. IIA and IIB or two isomeric species such as IIC and IID. The detection of *syn* and *anti* forms of $[Mo(CO)_2(\eta\text{-}C_5H_4Me)(\eta^5\text{-}C_5H_5)]^+$ by ^1H NMR spectroscopy [14] argues in favour of the former explanation but only by implication.

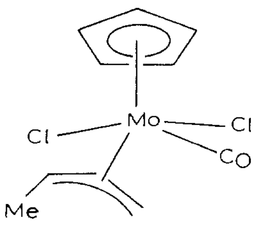
It is of interest to compare the relative reactivities of Group VI cyclopentadienyl metal tricarbonyl derivatives in reactions with allyl halides. Early studies by Fischer and co-workers established that $[Cr(CO)_3(\eta^5\text{-}C_5H_5)]_2$ and allyl bromide react photolytically in the presence of two electron donors L to give $[CrBr_2(L)(\eta^5\text{-}C_5H_5)]$ (L = THF, dioxane, EtO, pyridine, PPh_3 or acetone) [9]. Initial formation of $[CrBr(CO)_3(\eta^5\text{-}C_5H_5)]$ in these reactions seems probable, and this subsequently undergoes oxidation to the dibromide on further reaction with allyl bromide. This is



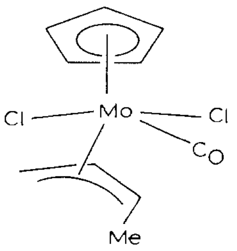
(IIA)



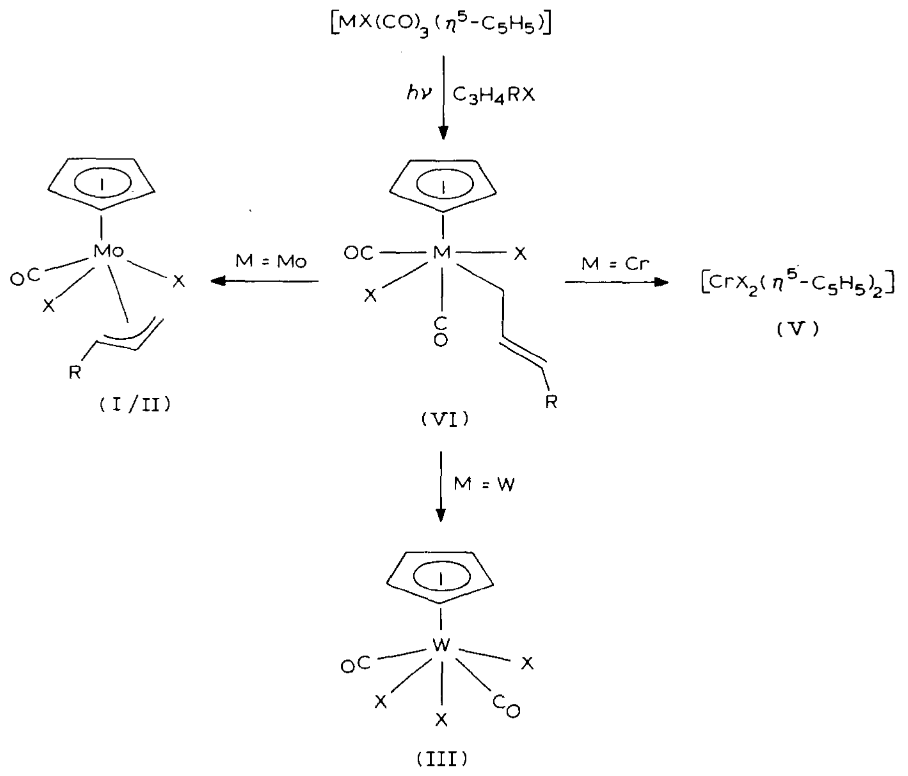
(IIB)



(IIC)



(IID)



SCHEME 1

suggested by the fact that the molybdenum and tungsten dimers $[M(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ react photolytically with carbon tetrachloride to give $[MCl(CO)_3(\eta^5\text{-}C_5H_4Me)]$ [5], coupled with our observation that $[CrI(CO)_3(\eta^5\text{-}C_5H_5)]$ reacts with allyl chloride to give $[CrCl_2(\eta^5\text{-}C_5H_5)]_2$. However, $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ only loses two CO ligands to give allylic derivatives I and II, whereas the tungsten derivative loses a single CO on oxidation to give the trihalides III.

Photolytic studies of $[MCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo, W), in coordinating solvents such as dimethyl sulphoxide have provided evidence for CO loss as the primary photochemical process rather than the alternative fission of the metal–halogen bond [15]. This and the isolation of $[W(CH_2Ph)Cl_2(CO)_2(\eta^5\text{-}C_5H_5)]$ from the photochemical reaction of $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with benzyl chloride [5] suggests a mechanism for the reaction of allyl and crotyl halides with $[MCl(CO)_3(\eta^5\text{-}C_5H_5)]$ involving CO dissociation, oxidative addition to yield an $\eta^1\text{-}C_3H_4R$ intermediate and, depending on the metal, three alternative reaction pathways to the observed products (see Scheme 1). Tyler [5] has proposed a related scheme to account for the formation of IIIa from the reaction of $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with CCl_4. The transformation of an intermediate CCl_3 derivative into the final product was thought to proceed via CO loss to give a carbenoid derivative (eqs. 1 and 2).

$$[WCCl_3Cl_2(CO)_2(\eta^5\text{-}C_5H_5)] \xrightarrow{-CO} [WCl_3(CCl_2)CO(\eta^5\text{-}C_5H_5)] \tag{1}$$

$$[WCl_3(CCl_2)CO(\eta^5\text{-}C_5H_5)] \xrightarrow{+CO} [WCl_3(CO)_2(\eta^5\text{-}C_5H_5)] \tag{2}$$

TABLE 1
SPECTROSCOPIC DATA FOR THE COMPLEXES

		IR $\nu(CO)$ (cm^{-1})		^1H NMR [a]	
				$\delta(C_5H_5)$	$\delta(C_3H_4R)$
$[MoCl_2(CO)(\eta^3-C_3H_5)(\eta^5-C_5H_5)]$	(Ia)	2034s		5.75s	5.85 (m,1H) 4.40 (d, *J* 137,1H) 4.20 (m,1H) 3.69 (dd, *J* 3.7 and 13.1,1H) 3.20 (dd, *J* 3.1 and 8.1, 1H)
$[MoBr_2(CO)(\eta^3-C_3H_5)(\eta^5-C_5H_5)]$	(Ib)	2031s		5.74s	5.68 (m,1H) 4.66 (d, *J* 12.5,1H) 4.30 (m,1H), 4.09 (dd, *J* 3.7 and 13.0, 1H) 3.25 (dd, *J* 2.7 and 8.5, 1H)
$[MoI_2(CO)(\eta^3-C_3H_5)(\eta^5-C_5H_5)]$	(Ic)	2022s		5.72s [b]	5.76 (m,1H) 4.30 (d, *J* 12.7, 1H), 4.1 (m,1H) 3.54 (dd, *J* 3.5 and 13.0, 1H) 3.18 (dd, *J* 2.8 and 8.7, 1H)
$[MoCl_2(CO)(\eta^3-C_3H_4Me)(\eta^5-C_5H_5)]$	(IIa)	2024s	major isomer	5.53s	5.40 (m,1H) 5.06 (m,1H) 4.22 (dd, *J* 4.4, 7.9,1H) 3.54 (dd, *J* 4.4, 12.2, 1H) 1.66 (d, *J* 6.1,3H)
			minor isomer	5.66s	5.40 (m,2H) 3.85 (d, *J* 11.9, 1H) 2.87 (d, *J* 8.6, 1H) 2.42(d, *J* 6.3, 3H)
$[MoBr_2(CO)(\eta^3-C_3H_4Me)(\eta^5-C_5H_5)]$	(IIb)	2024s	major isomer	5.69s	(5.40 m,1H) 4.6 (m,1H) 4.11 (d, *J* 11.8, 1H) 2.96(d, *J* 8.4, 1H) 2.52(d, *J* 6.3,3H)
			minor isomer	5.53s	(5.4 m,2H), 4.36(m,1H) 3.96(dd, *J* 4.1 and 5.4, 1H) 1.60(d, *J* 5.2, 3H)
$[WCl_3(CO)_2(\eta^5-C_5H_4SiMe_3)]$		2098s, 2046s [c]		6.20 (m,2H) 5.66 (m,2H) 0.43 (s,9H)	

[a] $\delta(Me_4Si) = 0$ ppm. *J* in Hz. [b] In CD_2Cl_2. [c] In Nujol.

This was proposed on the basis that two of the halogens in the final product appeared to be derived from a single CCl_4 molecule. However, in reactions involving allyl halides the formation of trihalides III clearly requires intervention by two halocarbon molecules i.e. if the intermediate VI is involved further attack by a second molecule of $RCH{=}CHCH_2X$ is required to give the product. Such a conclusion also applies to the formation of the chromium complex V and molybdenum derivatives I and II when halogen exchange is involved. Presumably photoinduced CO loss from the σ-allyl intermediate VI (M = Mo) leads directly to the η^3-allyl product, which is resistant to further attack by a second molecule of allyl halide to give the trihalide III.

In all of these reactions it is significant that the nature of the halides bonded to the metal in the final products depends only on the organic halide and not on the nature of X in $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$. This requires halogen substitution at the metal at some stage in the reaction. Mixed halide derivatives are known e.g. $[WBrCl_2(CO)_2(\eta^5\text{-}C_5H_5)]$ has been isolated from the reaction of $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with $CBrCl_3$ [5]. Consequently it is not inconceivable that halide exchange occurs in the final stages of the reaction as a result of attack by allyl halide on complexes such as $[Mo(Cl)(X)(CO)(\eta^3\text{-}C_3H_4R)(\eta^5\text{-}C_5H_5)]$ and $[WClX_2(CO)_2(\eta^5\text{-}C_5H_5)]$. Studies currently in progress may enable us to reach definite conclusions on this matter.

Experimental

Reactions were carried out in thick glass reaction tubes fitted with a Rotaflo teflon stopcock. Solvents were dried over CaH_2 and distilled before use. Halides $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$ were prepared by literature methods [16] while allyl and crotyl halides were obtained commercially (BDH) and distilled before use. IR spectra were recorded in CH_2Cl_2 on a Perkin–Elmer 580, NMR spectra in $CDCl_3$ (unless stated otherwise) on a Bruker WP200SY and mass spectra on a Vacuum Generators updated AEI MS9. Photochemical reactions were carried out with a Hanovia medium pressure mercury lamp.

Reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl chloride

200 mg complex was dissolved in 50 cm^3 of allyl chloride and transferred to a glass tube fitted with a teflon stopcock. The solution was degassed by four freeze-thaw cycles and on warming the room temperature irradiated with a medium pressure mercury lamp for 15 h. Deep red crystals formed during this time and these were filtered off, washed with diethyl ether and dried. Yield of $[MoCl_2(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ (Ia) 130 mg, (61%), Found: C, 35.7; H, 3.3; Cl, 23.3. Calcd.: C, 35.88; H 3.32; Cl, 23.58%.

Reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl bromide

200 mg complex in 40 cm^3 allyl bromide were reacted as above and after 15 h 185 mg (77%) of deep red crystals of $[MoBr_2(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ (Ib) were obtained. Found: C, 26.5; H, 2.58; Br, 42.6. Calcd.: C, 27.69; H, 2.56; Br, 41.02%.

Reaction of $[MoBr(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl bromide

200 mg complex and 40 cm^3 allyl bromide similarly gave $[MoBr_2(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ (Ib) in 72% yield.

Reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl iodide

200 mg complex and 40 cm^3 allyl iodide similarly gave impure crystals of $[MoI_2(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ (Ic) identified by comparison of spectroscopic data (Table 1) with those of Ia and Ib.

Reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with crotyl chloride

200 mg complex was dissolved in 50 cm^3 diethyl ether and 130 mg (1/2 molar ratio) crotyl chloride added. After degassing the solution was irradiated for 13 h when red crystals formed. These were collected, washed with diethyl ether and dried to give 85 mg, (38%) of $[MoCl_2(CO)(\eta^3\text{-}C_3H_4Me)(\eta^5\text{-}C_5H_5)]$. Found: C, 37.7; H, 3.8; Cl, 22.0. Calcd.: C, 38.1; H, 3.81; Cl, 22.54%.

Reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with crotyl bromide

200 mg complex and 193 mg (1/2 molar ratio) crotyl bromide in 50 cm^3 diethyl ether were irradiated for 15 h. Work-up as above gave deep red crystals of $[MoBr_2(CO)(\eta^3\text{-}C_3H_4Me)(\eta^5\text{-}C_5H_5)]$, 92 mg (32%). Found: C, 29.3; H, 2.9; Br, 38.9. Calcd.: C, 29.7; H, 2.97; Br, 39.6%.

Reaction of $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl chloride

300 mg complex and 40 cm^3 allyl chloride were irradiated for 15 h when a yellow solid formed. This was filtered off, washed with diethyl ether and dried to give 144 mg (43%) of $[WCl_3(CO)_2(\eta^5\text{-}C_5H_5)]$. Found: C, 20.7; H, 1.5; Cl, 25.3. Calcd.: C, 20.41; H, 1.22; Cl, 25.88%.

Reaction of $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl bromide

350 mg complex in 40 cm^3 allyl bromide were irradiated for 4 h when yellow crystals formed. Work-up as above gave $[WBr_3(CO)_2(\eta^5\text{-}C_5H_5)]$, 300 mg (58%). Found: C, 15.7; H, 0.9; Br, 43.4. Calcd.: C, 15.44; H, 0.92; Br, 44.12%.

Reaction of $[WCl(CO)_3(\eta^5\text{-}C_5H_4SiMe_3)]$ with allyl chloride

200 mg complex and 45 cm^3 allyl chloride were irradiated for 14 h when a yellow solid formed. Work-up as above gave 190 mg (85%) of $[WCl_3(CO)_2(\eta^5\text{-}C_5H_4SiMe_3)]$. Found: C, 24.2; H, 2.6; Cl, 22.4. Calcd.: C, 24.8; H, 2.7; Cl. 22.0%.

Reaction of $[CrI(CO)_3(\eta^5\text{-}C_5H_5)]$ with allyl chloride

200 mg complex and 40 cm^3 allyl chloride were irradiated for 15 h when lustrous blue crystals formed. These were filtered off, washed with diethyl ether and dried to give 31 mg (27%) of $[CrCl_2(\eta^5\text{-}C_5H_5)]$. Found: C, 32.3; H, 2.8; Cl, 36.47. Calcd.: C, 31.91; H, 2.66; Cl, 37.77%.

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