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REACTIONS OF METAL CARBONYL DERIVATIVES

XXIV *. MECHANISM OF HALOGENATION OF THE NON-BRIDGED METAL—METAL BONDED DERIVATIVES, $[\{M(\eta\text{-}C_5H_5)(CO)_2L\}_2]$ (M = Mo OR W, L = CO; M = Mo, L = $P(OCH_3)_3$) **

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Summary

Treatment of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (M = Mo or W) with diiodine in ethanol at 0°C in the presence of $Na[B(C_6H_5)_4]$ produces the iodide-bridged derivative $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}I)][B(C_6H_5)_4]$ (IV-$B(C_6H_5)_4$). IV is an intermediate in the formation of $[M(\eta\text{-}C_5H_5)(CO)_3I]$ from $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ and I_2 in dichloromethane as shown by monitoring with IR and, consistent with this, iodide attack on this bridged species gives $[M(\eta\text{-}C_5H_5)(CO)_3I]$. IV is also susceptible to nucleophilic attack by neutral donors such as acetone, pyridine, $P(C_6H_5)_3$ and $P(OCH_3)_3$. The reaction of the substituted derivatives $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ with an equimolar amount of diiodine in ethanol in the presence of $Na[B(C_6H_5)_4]$ also affords a bridged iodo product, viz. $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2(\mu\text{-}I)[B(C_6H_5)_4]$ although if an excess of diiodine is employed the molybdenum(IV) species $[Mo(\eta\text{-}C_5H_5)(CO)P(OCH_3)_3I_3]$ is formed. Bromination and chlorination of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ and $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ always gives rise to molybdenum(IV) derivatives, $[M(\eta\text{-}C_5H_5)(CO)_2X_3]$ or $[Mo(\eta\text{-}C_5H_5)(CO)P(OCH_3)_3X_3]$, as well as the molybdenum(II) products $[M(\eta\text{-}C_5H_5)(CO)_3X]$ or $[Mo(\eta\text{-}C_5H_5)(CO)_2\text{-}P(OCH_3)_3X]$ (X = Br or Cl), irrespective of the molar ratios employed. The tertiary phosphinemolybdenum(IV) compounds $[Mo(\eta\text{-}C_5H_5)(CO)LX_3]$ {L = $P(C_2H_5)_3$ or $P(CH_3)_2C_6H_5$, L ≠ $P(C_6H_5)_3$; X = Cl, Br or I} are produced by

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[*] For Part XXIII, see ref. 1, and for a preliminary communication, see ref. 2.

[**] Dedicated to Professor Joseph Chatt on the occasion of his 65th birthday, November 9th, 1979.

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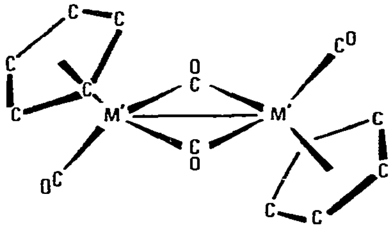
treatment of the corresponding molybdenum(II) derivatives [Mo(η-C_5H_5)-$(CO)_2LX$] with the appropriate dihalogen. A mechanism for the halogenation of [{M(η-C_5H_5)$(CO)_2L$}$_2$] (L = CO or $P(OCH_3)_3$) is proposed.

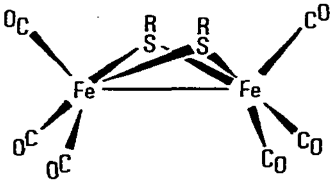
Introduction

Previous studies on the halogenation of metal—metal bonded dinuclear metal carbonyl complexes have indicated that, for [{M'(η-C_5H_5)$(CO)_2$}$_2$] (I; M' = Fe or Ru) [3—6], [{$Fe(CO)_3$(μ-SR)}$_2$] (II; R = alkyl or aryl group) and substituted



M' = Fe or Ru

(I)



(II)

derivatives of the latter [7,8], the reactions proceed via halide-bridged intermediates. For instance treatment of [{Fe(η-C_5H_5)$(CO)_2$}$_2$] with diiodine has been shown to lead to the formation of [{Fe(η-C_5H_5)$(CO)_2$}$_2$(μ-I)]$^+$ which reacts further with iodide ions to produce [Fe(η-C_5H_5)$(CO)_2I$] [5]. All of the compounds investigated contain either bridging carbonyl or bridging thiol groups [9—18] as shown * and even though the bridging carbonyls in [{M(η-C_5H_5)-$(CO)_2$}$_2$] are cleaved on halogenation [5,6], the bridging thiol groups in [{$Fe(CO)_3$(μ-SR)}$_2$], etc., remain intact [8]. On the basis of the results of these studies a general mechanism involving (i) electrophilic attack of the dihalogen molecule on the metal complex resulting in heterolytic cleavage of the halogen—halogen bond and the formation of the halide-bridged cationic intermediate and (ii) subsequent nucleophilic attack of the halide ion on the intermediate to give the neutral halide, was proposed.

To test the generality of the proposed scheme and in particular to establish whether it applies to non-bridged dinuclear species with fairly long metal—metal bonds, a study of the halogenation of [{M(η-C_5H_5)$(CO)_3$}$_2$] (III; M = Mo or W, L = CO) and the substituted derivative [{Mo(η-C_5H_5)$(CO)_2P(OCH_3)_3$}$_2$] {III; M = Mo, L = $P(OCH_3)_3$} has been made [21—24]. The Mo—Mo and W—W distances in [{Mo(η-C_5H_5)$(CO)_3$}$_2$] and [{W(η-C_5H_5)$(CO)_3$}$_2$] are 3.235(1) and 3.222(1) Å respectively [23]. These are much longer than those normally found for dinuclear compounds containing one or more bridging carbonyl groups [25,26].

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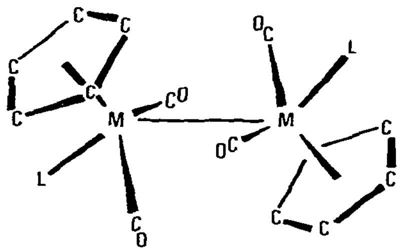
* Only the *trans*-bridged isomer of [{M'(η-C_5H_5)$(CO)_2$}$_2$] (M' = Fe or Ru) is illustrated. [{Fe(η-C_5H_5)$(CO)_2$}$_2$] is present primarily as a mixture of its *cis*- and *trans*-bridged isomers in solution [11,19], while [{Ru(η-C_5H_5)$(CO)_2$}$_2$] occurs in non-bridged forms in this phase as well as in the *cis*- and *trans*-bridged forms [9,10,14,20].



M = Mo or W

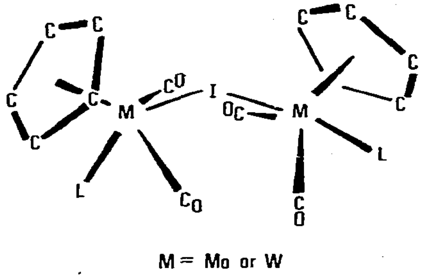
(III)

Results and discussion

In one of the earliest investigations involving $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ it was established that on reaction with diiodine in aromatic solvents such as benzene and toluene this compound gives rise to the neutral iodide, $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ [27]. Subsequent studies revealed that if an excess of diiodine is employed in these reactions the triiodide $[Mo(\eta\text{-}C_5H_5)(CO)_2I_3]$ is produced albeit very slowly [28,29]. The formation of the trihalide derivative was found to be much more rapid in the corresponding chlorination and bromination reactions however, so much so that the molybdenum(II) species $[Mo(\eta\text{-}C_5H_5)(CO)_3X]$ (X = Cl or Br) could not be isolated [28,29].

By monitoring the reactions of $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ and $[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$ with equimolar amounts of diiodine in dichloromethane by means of infrared spectroscopy we have observed that intermediates in the formation of $[M(\eta\text{-}C_5H_5)(CO)_3I]$ (M = Mo or W) can be detected. Their presence is short lived however and their C—O stretching peaks decreased in intensity with increase in intensity of the peaks corresponding to the neutral products; the decrease was found to be rapid for M = Mo but occurred at a more moderate rate for M = W. These intermediate species could nevertheless be isolated in moderate yield by performing the iodinations in the presence of $Na[B(C_6H_5)_4]$ in either ethanol at 0°C or toluene, plus sufficient ethanol to effect dissolution of the counterion, at —15°C. The compounds which separated from solution were characterised as the iodide-bridged derivatives $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}I)][B(C_6H_5)_4]$ (IV-$B(C_6H_5)_4$). The solution (CH_2Cl_2) and solid state IR spectra of these compounds reveal similar band patterns in the C—O stretching region with the better resolved solid state spectra exhibiting six peaks. Although this IR spectroscopic evidence cannot be employed for establishing the structure of these species it is consistent with the cations having a symmetry lower than C_{2v}. It is anticipated that these cations will have C_2 symmetry, as found for most compounds of the type $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}X)]$ (X = bridging group) [30].

IV was found to react very readily with iodide ions in solution to produce $[M(\eta\text{-}C_5H_5)(CO)_3I]$ indicating that this particular reaction is the final step in the formation of $[M(\eta\text{-}C_5H_5)(CO)_3I]$ from $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ and diiodine. The susceptibility of IV to iodide ion attack also explains our inability to obtain IV-$B(C_6H_5)_4$ in high yield or to isolate salts of IV employing other counterions such as $[N(C_4H_9)_4][PF_6]$.



(IV)

IV (M = Mo) was also found to be very susceptible to attack by neutral nucleophiles such as acetone, pyridine, triphenylphosphine and trimethyl phosphite. For instance on monitoring the dissolution of the tetraphenylborate salt of IV (M = Mo) in acetone-d_6 by means of ^{1}H NMR spectroscopy, it was observed that the resonance associated with the cyclopentadienyl protons of IV decreased in intensity with increase in intensity of two new cyclopentadienyl peaks, consistent with the fission of the Mo—I—Mo bridge and the formation of $[Mo(\eta\text{-}C_5H_5)(CO)_3(acetone)][B(C_6H_5)_4]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$. Whilst the neutral iodide was readily isolated from the reaction mixture, the acetone adduct was not owing to its slow decomposition in acetone solution and its rapid degradation in the absence of the solvent. It was thus identified by means of IR spectroscopy only.

Treatment of IV-$B(C_6H_5)_4$ (M = Mo) with pyridine in acetone or dichloromethane at room temperature led to the formation of $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ and an ionic product presumed to be $[Mo(\eta\text{-}C_5H_5)(CO)_3(py)][B(C_6H_5)_4]$ (py = pyridine) on the basis of its IR spectrum (see Table 2); its low solubility and its slow decomposition in solution prevented the measurement of its ^{1}H NMR spectrum and its isolation in pure form. Dissolution of IV-$B(C_6H_5)_4$ (M = Mo) in neat pyridine, on the other hand, resulted in the formation of the bis-substituted ionic product, $[Mo(\eta\text{-}C_5H_5)(CO)_2(py)_2][B(C_6H_5)_4]$, isolated as the *cis* (lateral) isomer according to IR evidence [31—34], as well as the neutral iodide $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$.

The reactions of IV-$B(C_6H_5)_4$ (M = Mo) with $P(C_6H_5)_3$ and $P(OCH_3)_3$ in acetone or dichloromethane at ambient temperature afforded not only $[Mo(\eta\text{-}C_5H_5)(CO)_3L][B(C_6H_5)_4]$ (L = $P(C_6H_5)_3$ or $P(OCH_3)_3$) and $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ but substituted derivatives thereof. Thus the reaction involving $P(C_6H_5)_3$ gave $[Mo(\eta\text{-}C_5H_5)(CO)_3P(C_6H_5)_3][B(C_6H_5)_4]$ [35], $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_2P(C_6H_5)_3I]$ [32,35] whilst that involving $P(OCH_3)_3$ produced $[Mo(\eta\text{-}C_5H_5)(CO)_3P(OCH_3)_3][B(C_6H_5)_4]$, $[Mo(\eta\text{-}C_5H_5)(CO)_2\{P(OCH_3)_3\}_2][B(C_6H_5)_4]$ [24], $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3I]$ [33,34]. No attempts were made to separate $[Mo(\eta\text{-}C_5H_5)(CO)_2\{P(OCH_3)_3\}_2][B(C_6H_5)_4]$ from $[Mo(\eta\text{-}C_5H_5)(CO)_3P(OCH_3)_3][B(C_6H_5)_4]$ and the two were identified by means of IR only: $[Mo(\eta\text{-}C_5H_5)(CO)_3P(OCH_3)_3][B(C_6H_5)_4]$: ν(C—O) 2071s, ca. 2010s and ca. 1990s cm^{-1}; $[Mo(\eta\text{-}C_5H_5)(CO)_2\{P(OCH_3)_3\}_2][B(C_6H_5)_4]$: ν(C—O) 1985ms and 1920s cm^{-1}, both in CH_2Cl_2. $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3I]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_2$-

$P(C_6H_5)_3I]$ which were both separated from $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ by means of column chromatography, were isolated as mixtures of their *cis*- (lateral) and *trans*-isomers (diagonal) [31—34]. IV-$B(C_6H_5)_4$ (M = Mo) was also found to react with diiodine in CH_2Cl_2 to produce $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$, but the rate of reaction was very much slower than that for the corresponding reaction involving iodide ions.

The reaction of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (M = Mo or W) with an excess of diiodine in CH_2Cl_2 was also monitored and, as established previously [28,29], the neutral iodide $[M(\eta\text{-}C_5H_5)(CO)_3I]$ was observed to react slowly with the excess diiodine to produce $[M(\eta\text{-}C_5H_5)(CO)_2I_3]$. In contrast to the iodination reactions, the bromination of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ in dichloromethane always afforded the metal(IV) products $[M(\eta\text{-}C_5H_5)(CO)_2Br_3]$ [28,29], via $[M(\eta\text{-}C_5H_5)(CO)_3Br]$, irrespective of the $Br_2/[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ molar ratio employed. $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}Br)]^+$ could not be detected in these reactions nor for that matter could it be isolated by performing the brominations in ethanol in the presence of a counterion. This is attributed to the rapid rate of formation of the two neutral products. The chlorination reactions of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ were found to be even more rapid than the corresponding brominations such that the neutral chloride $[M(\eta\text{-}C_5H_5)(CO)_3Cl]$ could not be detected in the formation of $[M(\eta\text{-}C_5H_5)(CO)_2Cl_3]$ even when less than equimolar quantities of dichlorine were employed.

A halide-bridged product was isolated from the reaction of the substituted derivative, $[\{M(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ [24], with an equi- or twice molar amount of diiodine in ethanol at 0°C, in the presence of $Na[B(C_6H_5)_4]$. This compound which was characterised as $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2(\mu\text{-}I)]$-$[B(C_6H_5)_4]$, afforded a ^1H NMR spectrum containing two C_5H_5 resonances of near equal intensity, one occurring as a singlet and the other as a doublet (J 2 Hz). A third much weaker resonance, possibly a doublet, was also discernible. Previous studies have shown that the C_5H_5 resonances in the ^1H NMR spectra of the *trans*-isomer (diagonal) of $[Mo(\eta\text{-}C_5H_5)(CO)_2LX]$ (L = ligand; X = Cl, Br or I) are split into doublets whereas those in the spectra of the *cis*-isomers (lateral) occur as singlets [33]. The NMR data are thus consistent with the $Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3$ moieties in $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2(\mu\text{-}I)]^+$ adopting both a *trans*- (diagonal) and a *cis*-configuration (lateral) but whether this species is present in solution as primarily the "*cis,trans*" isomer or as primarily a mixture of the "*cis,cis*" and "*trans,trans*" isomers in approximately equal amounts cannot be established from the available spectroscopic evidence.

In contrast to IV, $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3\}_2(\mu\text{-}I)][B(C_6H_5)_4]$ was found to be exceptionally stable to iodide ion attack. In fact even when a twenty-fold excess of iodide ions was employed there was no indication of any reaction having taken place after a period of 30 minutes. On the other hand the compound reacted fairly rapidly with diiodine to produce $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3I]$. This would explain the observation that reaction of $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ with an equimolar quantity of diiodine in CH_2Cl_2 gave primarily $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3I]$ together with a little $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2(\mu\text{-}I)]^+$. Utilisation of a large excess of diiodine in the iodination of $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ led to the formation of the molybdenum(IV) species, $[Mo(\eta\text{-}C_5H_5)(CO)P(OCH_3)_3I_3]$, best isolated from reactions employing benzene as solvent.

The reaction of $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ with dibromine and dichlorine always afforded the molybdenum(IV) products, $[Mo(\eta\text{-}C_5H_5)(CO)P(OCH_3)_3Br_3]$ and $[Mo(\eta\text{-}C_5H_5)(CO)P(OCH_3)_3Cl_3]$, irrespective of the molar ratios employed. $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3Br]$ [34] and $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3Cl]$ [34] were observed to be intermediates in the formation of these trihalide derivatives but the halide bridged species $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2(\mu\text{-}X)]^+$ (X = Br or Cl) could not be detected in solution. Deliberate attempts to synthesise the latter from $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ were also unsuccessful. The molybdenum(IV) compounds $[Mo(\eta\text{-}C_5H_5)(CO)P(OCH_3)_3X_3]$ (X = Cl, Br and I) decomposed rapidly in solution and thus could not be recrystallized without extensive decomposition. They were best obtained by reacting the molybdenum(II) halide $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3X]$ (X = Cl, Br or I) with the appropriate dihalogen in toluene (or toluene/CCl_4) at 0° C and allowing the product to crystallise directly from the reaction solution. The solid state IR spectra of these compounds revealed two well resolved peaks in the C—O stretching region suggesting an alternative formulation of $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3X_2]X$. This possibility was eliminated however on the basis of conductivity measurements and the presence of a single C—O stretching band, albeit fairly broad, in the dichloromethane IR spectra.

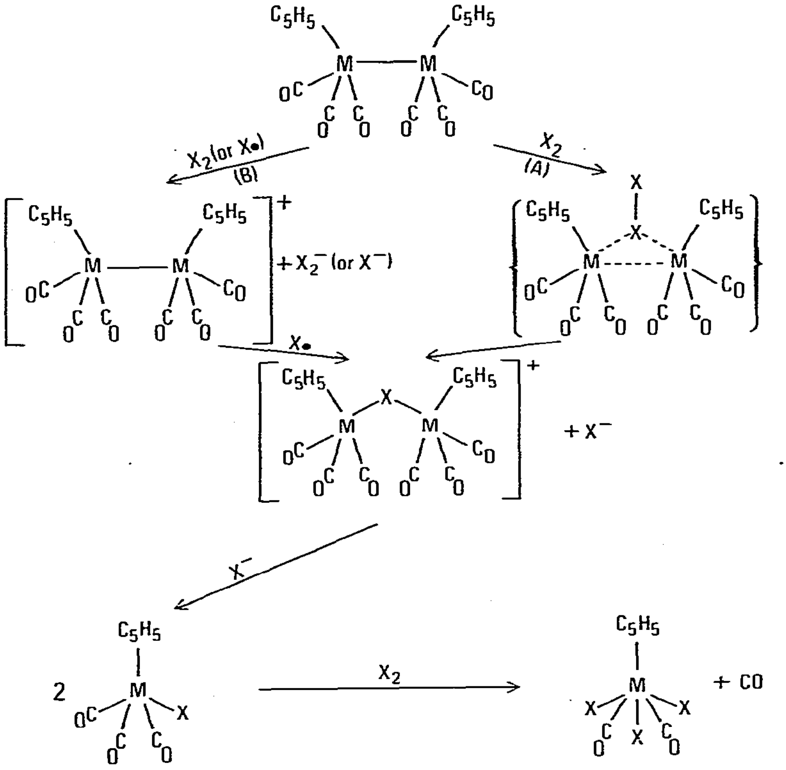
Treatment of $[Mo(\eta\text{-}C_5H_5)(CO)_2LX]$ (L = $P(C_2H_5)_3$ or $P(CH_3)_2C_6H_5$; X = Cl, Br or I) [32,33,36] with the appropriate dihalogen in benzene or benzene/CCl_4 also led to the formation of molybdenum(IV) products, viz. $[Mo(\eta\text{-}C_5H_5)(CO)LX_3]$. Similar to $[Mo(\eta\text{-}C_5H_5)(CO)P(OCH_3)_3X_3]$, these compounds were found to be unstable in solution and could not be purified by crystallisation; in the case of the triiodides, the rate of decomposition was such that they could not be isolated. Interestingly these molybdenum(IV) derivatives also afforded solid state IR spectra containing two C—O stretching modes. The triphenylphosphine-substituted derivatives $[Mo(\eta\text{-}C_5H_5)(CO)_2P(C_6H_5)_3X]$ (X = Cl, Br or I) [32,35] were also observed to react with dihalogens but the products were found to be the dicarbonyl species $[Mo(\eta\text{-}C_5H_5)(CO)_2X_3]$. The formation of the latter instead of $[Mo(\eta\text{-}C_5H_5)(CO)P(C_6H_5)_3X_3]$ is attributed to the relatively large steric bulk of the triphenylphosphine ligand [37].

Mechanism of halogenation

It is apparent from the above results that halogenation of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (M = Mo or W) occurs via a pathway (or pathways) analogous to that (or those) for $[\{M'(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (M' = Fe or Ru) with the penultimate step in the reaction scheme being a simple nucleophilic substitution involving halide ion attack on $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}X)]^+$ (X halogen) as shown (Scheme 1); the final step, which does not have a counterpart in the corresponding $[\{M'(\eta\text{-}C_5H_5)(CO)_2\}_2]$ halogenations, involves carbonyl replacement and oxidative addition of the dihalogen molecule.

The formation of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}X)]^+$ is proposed to occur via one of two pathways, or both. The one (pathway A) involves electrophilic attack by the dihalogen at metal sites of the complex leading to heterolytic cleavage of the halogen—halogen bond and the formation of the halide-bridged species through a three-centre transition state as shown. This pathway is analogous to that generally accepted for the electrophilic addition of halogens to olefins [38,39].

SCHEME 1



M = Mo or W; X = Cl, Br or I

The other pathway (B) is suggested in the light of some recent studies by McCleverty et al. and by Connelly et al. The former discovered that reaction of $[\{Fe(CO)_3(\mu\text{-}SR)\}_2]$ (R = CH_3, C_2H_5 or C_6H_5) with $(CF_3)_2C_2S_2$ afforded, quite unexpectedly, $[Fe_2(CO)_6(\mu\text{-}SR)_3]^+$ [40,41]. A detailed study of this reaction, as well as that of $[\{Fe(CO)_3(\mu\text{-}SR)\}_2]$ with $[NO]PF_6$ in the presence of $(RS)_2$, revealed that the tris-mercapto-bridged species is produced by formal insertion of a $RS^\bullet$ radical into the iron—iron bond of $[\{Fe(CO)_3(\mu\text{-}SR)\}_2]^+$; the latter is formed by one-electron oxidation of $[\{Fe(CO)_3(\mu\text{-}SR)\}_2]$ by $[\{(Fe\{(CF_3)_2C_2S_2\}_2\}_2]$ or $[NO]PF_6$ [40]. Connelly et al. reported more recently [42] that treatment of $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}SC_6H_4CH_3\text{-p})\}_2]$ with $[NO]PF_6$ in the presence of $(p\text{-}CH_3C_6H_4S)_2$ affords $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}SC_6H_4CH_3\text{-}p)_3]^+$ and on the basis of theirs and the results of McCleverty et al. suggested that the formation of $[\{Fe(CO)_2L(\mu\text{-}SR)\}_2(\mu'\text{-}I)]^+$ (L = tertiary phosphine, R = alkyl or aryl group) in the reaction of $[\{Fe(CO)_2L(\mu\text{-}SR)\}_2]$ with iodine [7,8] occurs via a pathway involving insertion of an iodine radical, $I^\bullet$, into the iron—iron bond of $[\{Fe(CO)_2L(\mu\text{-}SR)\}_2]^+$. Pathway B will involve electron transfer from $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ to X_2 (or $X^\bullet$) through the coordinated cyclopentadienyl or carbonyl groups followed by fission of X_2 to X^- and $X^\bullet$. Consistent with this mode of attack is a recent communication describing some kinetic studies on the reactions of Br_2 and I_2 with several substituted derivatives of $[\{Mn(CO)_5\}_2]$ and $[\{Re(CO)_5\}_2]$ [43]. These indicated that initial attack by the dihalogens occurred at the extremities of the carbonyl ligands. With the object of ascertaining the feasibility of the formation of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2\text{-}(\mu\text{-}X)]^+$ occurring via pathway B, $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ was treated with $[NO]PF_6$ in the presence of $(C_6H_5S)_2$. No $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}SC_6H_5)]^+$ could be detected in solution however.

A number of alternative mechanisms for the halogenation of $[\{M(\eta\text{-}C_5H_5)\text{-}(CO)_3\}_2]$ were also considered but in each case were readily eliminated. For instance it has been established that $M(\eta\text{-}C_5H_5)(CO)_3^{\bullet}$ radicals are readily generated from $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ under photochemical conditions [44—46] *, but a radical mechanism involving $M(\eta\text{-}C_5H_5)(CO)_3^{\bullet}$ would not readily explain the formation of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}X)]^+$. A second possibility involving the heterolytic fission of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ according to equations 1—5 was discarded on the basis that only $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}I)]^+$

$$[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2] \rightleftharpoons [M(\eta\text{-}C_5H_5)(CO)_3]^+ + [M(\eta\text{-}C_5H_5)(CO)_3]^- \tag{1}$$

$$[M(\eta\text{-}C_5H_5)(CO)_3]^- + X_2 \rightarrow [M(\eta\text{-}C_5H_5)(CO)_3X] + X^- \tag{2}$$

$$[M(\eta\text{-}C_5H_5)(CO)_3]^+ + X^- \rightarrow [M(\eta\text{-}C_5H_5)(CO)_3X] \tag{3}$$

$$[M(\eta\text{-}C_5H_5)(CO)_3]^+ + [M(\eta\text{-}C_5H_5)(CO)_3X] \rightarrow [\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}X)]^+ \tag{4}$$

$$[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}X)]^+ + X^- \rightarrow 2\ [M(\eta\text{-}C_5H_5)(CO)_3X] \tag{5}$$

(M = Mo or W) was observed to be formed in the initial stages of the iodination of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ and that $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ failed to react with an equimolar amount of $P(C_6H_5)_3$ in ethanol over a period of 12 h.

No single mechanism can be proposed for the halogenation of $[\{Mo(\eta\text{-}C_5H_5)\text{-}(CO)_2P(OCH_3)_3\}_2]$ on the basis of the data presently available. It is clear that $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2(\mu\text{-}I)]^+$ is an intermediate in the formation of $[Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3I]$ but iodine and not iodide ion attack on the bridged species gives rise to the latter. Alternative pathways very different from those represented in Scheme 1 cannot be eliminated at this stage and kinetic studies using the stopped-flow technique are required before a firm proposal can be made.

It is apparent from our studies on the halogenation of a range of dinuclear metal—metal bonded compounds [3,5,6,8,47,48] that the mechanistic pathways depicted in Scheme 1 are common to a number of dinuclear systems and probably apply to the halogenation of a much wider range of compounds than those studied. Our earlier reports did not however consider pathway B as a possibility in the formation of the halide-bridged species. This pathway will certainly explain the intermediacy of $[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ in the formation of $[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(\mu\text{-}I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ from $[\{Fe(\eta\text{-}C_5H_5)(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]$ and excess of diiodine [48], will account for the second pathway used to explain the formation of $[Fe(\eta\text{-}C_5H_5)\text{-}(CO)_2L]^+$ (L = tertiary phosphine or phosphite), as well as $[Fe(\eta\text{-}C_5H_5)(CO)LI]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$, by iodination of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3L]$ [47] and will

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* These radicals react readily with chlorocarbon trapping agents to produce $[M(\eta\text{-}C_5H_5)(CO)_3Cl]$ [44,46].

explain as readily as pathway A the formation of $[\{M'(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}X)]^+$ (M' = Fe or Ru) * and $[\{Fe(CO)_2L(\mu\text{-}SR)\}_2(\mu'\text{-}X)]^+$ in the respective halogenation and iodination reactions of $[\{M'(\eta\text{-}C_5H_5)(CO)_2\}_2]$ and $[\{Fe(CO)_2L(\mu\text{-}SR)\}_2]$ [3,5,6,8]. On the other hand a pathway analogous to A is much more appropriate for describing the insertion of H^+ into the Fe—Fe bond in $[\{Fe(CO)_2L(\mu\text{-}SCH_3)\}_2]$ (L = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$) $P(CH_3)(C_6H_5)_2$ or $P(C_6H_5)_3$) [51] and of $SnCl_2$ into the Fe—Fe bonds of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OC_6H_5)_3]$ affording $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}SnCl_2)]$ [52] and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3P(OC_6H_5)_3(\mu\text{-}SnCl_2)]$ [53], respectively.

Experimental

$[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (M = Mo and W) [54,55] $[Mo(\eta\text{-}C_5H_5)(CO)_3X]$ (X = Cl, Br and I) [27,44,56], $[Mo(\eta\text{-}C_5H_5)(CO)_2LX]$ {X = Cl, Br and I; L = $P(OCH_3)_3$, $P(C_2H_5)_3$, $P(CH_3)_2C_6H_5$ and $P(C_6H_5)_3$} [32—34,36] and $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ [24] were synthesised according to literature methods while $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ was also obtained commercially. All reactions and operations were carried out under an atmosphere of dinitrogen. The chromatographic separations were effected on an alumina column (50 × 1.5 cm; Merck acid washed alumina, activity III). The IR and NMR spectra were recorded on a Perkin—Elmer model 457 spectrophotometer and on Varian T60 and FT80A instruments, respectively. Microanalytical results were obtained commercially.

Physical properties and the analytical data of the compounds synthesised are summarized in Table 1.

Synthesis of $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}I)].[B(C_6H_5)_4]$ *(M = Mo or W)*

A solution of diiodine (0.50 g, 2.0 mmol) in ethanol (ca. 50 ml) was added dropwise to a stirred solution of $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (0.98 g, 2.0 mmol) or $[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (1.33 g, 2.0 mmol) and $Na[B(C_6H_5)_4]$ (1.03 g, 3.0 mmol) in ethanol (ca. 50 ml) at 0°C. The reaction mixture was stirred for a further hour at this temperature and then centrifuged. The residue was washed in turn with small portions of benzene, chloroform, water and ethanol and then extracted with dichloromethane. The extract was filtered and the filtrate evaporated to dryness to afford the title compound as a brown microcrystalline solid which was washed successively with chloroform, benzene and petroleum ether and dried thoroughly. Yields: $[\{Mo(\eta\text{-}C_5H_5)(CO)_3)_2(\mu\text{-}I)][B(C_6H_5)_4]$: ca. 50%; $[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}I)][B(C_6H_5)_4]$: ca. 33%.

Synthesis of $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2(\mu\text{-}I)][B(C_6H_5)_4]$

The title compound was synthesised from $[\{Mo(\eta\text{-}C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ (1.02 g, 1.5 mmol) and diiodine (0.38 g, 1.5 mmol) in ethanol at 0°C in the presence of $Na[B(C_6H_5)_4]$ (0.68 g, 2.0 mmol) and purified according to the method described above omitting the chloroform washing step. Yield: ca. 30%.

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* Although $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ can be readily oxidised to $[Fe(\eta\text{-}C_5H_5)(CO)_2(solvent)]^+$ in acetone or acetonitrile, probably via $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]^+$ [49], reaction of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ with $[NO]PF_6$ in CH_2Cl_2 in the presence of $(C_6H_5S)_2$ did not afford $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}SC_6H_5)]^+$ [50]. This is not consistent with pathway B.

TABLE 1

COLOURS AND CONDUCTIVITY AND ANALYTICAL DATA

Compound [a]	Colour	Conductivity [b]	Analyses (Found (calcd.) (%))			
		ohm^{-1} cm^2 mol^{-1}	C	H	Others	
$[Mo(Cp)(CO)_2P(OMe)_3Cl]$	Orange	0.73	32.4 (31.9)	4.0 (3.8)		
$[Mo(Cp)(CO)_2P(OMe)_3Br]$	Orange	0.79	28.9 (28.5)	3.2 (3.4)		
$[Mo(Cp)(CO)_2P(OMe)_3I]$	Red	0.88	25.7 (25.7)	3.1 (3.0)		
$[Mo(Cp)(CO)_2PPh_3I]$	Red	0.93	49.6 (49.5)	3.2 (3.3)		
$[\{Mo(Cp)(CO)_3\}_2I][BPh_4]$	Brown	86	51.1 (51.3)	3.2 (3.2)	I,	13.8 (13.6)
$[\{W(Cp)(CO)_3\}_2I][BPh_4]$	Brown	108	43.2 (43.2)	2.9 (2.7)	I,	10.6 (11.4)
$[\{Mo(Cp)(CO)_2P(OMe)_3\}_2I][BPh_4]$	Red brown	103	46.2 (46.8)	4.3 (4.3)	I,	10.8 (11.2)
$[Mo(Cp)(CO)_3PPh_3][BPh_4]\cdot\frac{1}{2}CH_2Cl_2$	Yellow	104	70.1 (69.8)	4.8 (4.8)		
$[Mo(Cp)(CO)_3PPh_3][BPh_4]$	Red	115	70.0 (70.9)	5.1 (5.1)	N,	3.5 (4.0)
$[Mo(Cp)(CO)P(OMe)_3Cl_3]$	Orange	18	24.3 (25.8)	3.4 (3.4)	Cl,	24.4 (25.3)
$[Mo(Cp)(CO)P(OMe)_3Br_3]$	Orange	4.5	20.2 (19.6)	2.4 (2.6)	Br,	42.0 (43.4)
$[Mo(Cp)(CO)PMe_2PhCl_3]$	Orange	6.1	38.3 (38.8)	3.8 (3.8)	Cl,	24.2 (24.5)
$[Mo(Cp)(CO)PMe_2PhBr_3]$	Orange	5.5	28.7 (29.7)	2.7 (2.8)	Br,	41.9 (42.3)
$[Mo(Cp)(CO)PEt_3Cl_3]$	Brown	5.8	33.6 (34.9)	5.0 (4.9)	Cl,	25.4 (25.7)
$[Mo(Cp)(CO)PEt_3Br_3]$	Brown	6.8	26.1 (26.4)	3.8 (3.7)	Br,	43.9 (43.8)

[a] Abbreviations: Cp, η-C_5H_5; Me, CH_3; Et, C_2H_5; Ph, C_6H_5; Py, pyridine. [b] 1—10 × 10^{-4} M solutions in acetone.

Reaction of $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}I)]^+$ with various nucleophiles, L

A solution of pyridine (0.05 g, 0.63 mmol) or $P(OCH_3)_3$ (0.08 g, 0.65 mmol) or $P(C_6H_5)_3$ (0.15 g, 0.57 mmol) or $[N(C_4H_9)_4]I$ (0.20 g, 0.54 mmol) in CH_2Cl_2 (ca. 30 ml) was added dropwise to a stirred solution of $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2(\mu\text{-}I)][B(C_6H_5)_4]$ (0.51 g, 0.5 mmol) in CH_2Cl_2 (ca. 80 ml) at ambient temperature. The solution was stirred for a further 15 min to 3 h and the solvent removed under reduced pressure. The residue was purified as follows:

L = pyridine. The residue was extracted with benzene and filtered. The insoluble residue was identified as $[Mo(\eta\text{-}C_5H_5)(CO)_3py][B(C_6H_5)_4]$ by means of IR spectroscopy only. IR was also employed to establish the presence of $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ in the benzene extract.

L = $P(OCH_3)_3$. The residue was extracted with benzene and the extract filtered. The filtrate was concentrated to a small volume and transferred to an alumina column. $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ was removed from the column by eluting with benzene/petroleum ether (1/6). A second red band was obtained by elut-

TABLE 2

IR AND NMR SPECTROSCOPIC DATA

Compound	CO stretching frequencies ^{a} (cm^{-1})	Proton resonances ^{b}	
		C_5H_5	CH_3
$[\mathrm{Mo(Cp)(CO)_3Cl}]$	2055ms, 1983s, 1960s ^{h}	4.25 ^{n}	
$[\mathrm{W(Cp)(CO)_3Cl}]$	2042ms, 1955s(br) ^{i}	n.m.	
$[\mathrm{Mo(Cp)(CO)_3Br}]$	2050ms, 1980s, 1960s ^{h}	4.29s ^{n}	
$[\mathrm{W(Cp)(CO)_3Br}]$	2040ms, 1953s(br) ^{i}	n.m.	
$[\mathrm{Mo(Cp)(CO)_3I}]$	2042ms, 1973s, 1959s ^{h}	4.39s ^{n}	
$[\mathrm{W(Cp)(CO)_3I}]$	2037ms, 1952s(br) ^{i}	n.m.	
$[\mathrm{Mo(Cp)(CO)_2P(OMe)_3Cl}]$ ^{c}	1985s, 1902m ^{h}	4.48s $^{j, n}$	6.24d [J(PH) 12.0 Hz]
$[\mathrm{Mo(Cp)(CO)_2P(OMe)_3Br}]$ ^{d}	1982s, 1901m ^{h}	4.48s $^{j, n}$	6.23d [J(PH) 11.7 Hz]
		4.62d [J(PH) 2 Hz] ^{k}	
$[\mathrm{Mo(Cp)(CO)_2P(OMe)_3I}]$ ^{e}	1981m, 1901s ^{h}	4.55s $^{j, n}$	6.26d [J(PH) 11.8 Hz]
		4.65d [J(PH) 2 Hz] ^{k}	
$[\mathrm{Mo(Cp)(CO)_2PPh_3Cl}]$ ^{c}	1969s, 1881ms ^{i}	4.60s $^{j, n}$	
$[\mathrm{Mo(Cp)(CO)_2PPh_3Br}]$ ^{c}	1969s, 1880ms ^{i}	4.60s $^{j, n}$	
$[\mathrm{Mo(Cp)(CO)_2PPh_3I}]$ ^{f}	1966ms, 1885s ^{i}	4.65s $^{j, n}$	
		4.89d [J(PH) 2 Hz] ^{k}	
$[\mathrm{Mo(Cp)(CO)_2PMe_2PhCl}]$ ^{c}	1979s, 1881ms ^{h}	4.63s $^{j, n}$	8.08d [J(PH) 9.6 Hz]
			8.11d [J(PH) 9.6 Hz]
$[\mathrm{Mo(Cp)(CO)_2PMe_2PhBr}]$ ^{c}	1978s, 1881ms ^{h}	4.66s $^{j, n}$	8.02d [J(PH) 9.8 Hz]
			8.07d [J(PH) 9.8 Hz]
$[\mathrm{Mo(Cp)(CO)_2PMe_2PhI}]$ ^{g}	1974s, 1880ms $^{j, h}$	4.69s $^{j, n, o}$	7.87d [J(PH) 9.6 Hz]
			7.91d [J(PH) 9.6 Hz]
	1959m, 1876s $^{k, i}$		
$[\mathrm{Mo(Cp)(CO)_2PEt_3Cl}]$ ^{c}	1971s, 1880ms ^{h}	4.56s $^{j, n}$	8.90d of t [J(PH) 14.6 Hz; J(HH) 6.2 Hz]
$[\mathrm{Mo(Cp)(CO)_2PEt_3Br}]$ ^{c}	1973s, 1883ms ^{h}	4.59 $^{j, n}$	8.93d of t [J(PH) 14.0 Hz; J(HH) 7.0 Hz]
$[\mathrm{Mo(Cp)(CO)_2PEt_3I}]$ ^{g}	1969s, 1884m $^{j, h}$	4.62s $^{j, n, o}$	8.93d of t [J(PH) 14.4 Hz; J(HH) 7.0 Hz]
	1955m, 1868s $^{k, i}$		
$[\{\mathrm{Mo(Cp)(CO)_3}\}_2\mathrm{I}][\mathrm{BPh_4}]$	2055s, 2040m, 1984s, 1976s, 1957s, 1948s ^{l}	4.74s ^{p}	
	2071ms, 2059ms, 1995ip, 1980s, 1960ip ^{i}		
$[\{\mathrm{W(Cp)(CO)_3}\}_2\mathrm{I}][\mathrm{BPh_3}]$	2050s, 2038m, 1972s, 1962s, 1941s, 1930s ^{l}	4.50 ^{p}	
	2059m, 2045ms, 1979ip, 1966s, 1949ip ^{i}		
$[\{\mathrm{Mo(Cp)(CO)_2P(OMe)_3}\}_2\mathrm{I}][\mathrm{BPh_4}]$	1978(sh), 1964s, 1902s, 1882s ^{l}	4.61s ^{n}	6.37d [J(PH) 12.0 Hz]
	1995(sh), 1981ms, 1915(sh), 1902s ^{i}	4.78d [J(PH) 2 Hz]	6.40d [J(PH) 12.0 Hz]

TABLE 2 (continued)

Compound	CO stretching frequencies [a] (cm^{-1})	Proton resonances [b]	
		C_5H_5	CH_3
[Mo(Cp)(CO)$_3$(acetone)][BPh$_4$]	2055s, ca. 1965s(br) [m]	4.52 [p]	
[Mo(Cp)(CO)$_3$Py][BPh$_4$]	2065s, 2000s, 1974s [i]	n.m.	
[Mo(Cp)(CO)$_3$PPh$_3$][BPh$_4$]	2061s, 2000ms, 1978s [l]	5.13 [n]	
[Mo(Cp)(CO)$_2$(Py)$_2$][BPh$_4$]	1997s, 1880s [i]	n.m.	
Mo(Cp)(CO)$_2$Cl$_3$]	2104ms, 2062s [l]	n.m.	
[W(Cp)(CO)$_2$Cl$_3$]	2097ms, 2048s [l]	n.m.	
[Mo(Cp)(CO)$_2$Br$_3$]	2092ms, 2058s [i]	n.m.	
[W(Cp)(CO)$_2$Br$_3$]	2084ms, 2041s [i]	n.m.	
[Mo(Cp)(CO)$_2$I$_3$]	2065ms, 2037s [l]	n.m.	
[W(Cp)(CO)$_2$I$_3$]	2068ms, 2025s [i]	n.m.	
[Mo(Cp)(CO)P(OMe)$_3$Cl$_3$]	2045 [i] 2038s, 2020sh [q]	4.27s(br) [l]	6.02d [J(PH) 10.6 Hz]
[Mo(Cp)(CO)P(OMe)$_3$Br$_3$]	2039 [i] 2052m, 2032s [l]	4.07s [q]	6.01d [J(PH) 10.0 Hz]
[Mo(Cp)(CO)P(OMe)$_3$I$_3$]	2018 [i] 1997s [l]	i.s. [r]	
[Mo(Cp)(CO)PMe$_2$PhCl$_3$]	2031 [i] 2028sh, 2012s [l]	i.s. [r]	
[Mo(Cp)(CO)PMe$_2$PhBr$_3$]	2017 [i] 1993s, 1984s [l]	i.s. [r]	
[Mo(Cp)(CO)PMe$_2$PhI$_3$]	1997 [i]	i.s. [r]	
[Mo(Cp)(CO)PEt$_3$Cl$_3$]	2023 [i] 2042sh, 2010s [l]	i.s. [r]	
[Mo(Cp)(CO)PEt$_3$Br$_3$]	2017 [i] 2016sh, 1999s [l]	i.s. [r]	

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[a] Abbreviations: m, medium; ms, medium strong; s, strong; (br), broad; (sh), shoulder; ip, inflection point. [b] τ scale relative to TMS. Abbreviations: s, singlet; d, doublet; t, triplet; (br), broad; n.m., not measured; i.s., insufficiently soluble. [c] Isolated as a single isomer. [d] Isolated as a mixture of isomers, 75% *cis* and 25% *trans*. [e] Isolated as a mixture of isomers, 35% *cis* and 65% *trans*. [f] Isolated as a mixture of isomers, 50% *cis* and 50% *trans*. [g] Isolated in two isomeric forms. [h] Measured in C_6H_{12}. [i] Measured in CH_2Cl_2. [j] *cis*-Isomer. [k] *trans*-Isomer. [l] Measured as a nujol mull. [m] Measured in acetone. [n] Measured in $CDCl_3$. [o] *trans*-Isomer not measured. [p] Measured in CD_3COCD_3. [q] Measured in CD_2Cl_2. [r] Sample decomposed too rapidly for FTNMR measurement.

ing with 1/3 benzene/petroleum ether. Evaporation of the eluate and crystallisation of the residue from ether yielded red crystals of [Mo(η-C_5H_5)$(CO)_2$-$P(OCH_3)_3I$]. The residue from the filtration was shown to be a mixture of [Mo(η-C_5H_5)$(CO)_3P(OCH_3)_3$][$B(C_6H_5)_4$] and [Mo(η-C_5H_5)$(CO)_2\{P(OCH_3)_3\}_2$]-[$B(C_6H_5)_4$] by means of IR.

L = *P*(C_6H_5)$_3$. The residue was extracted with benzene and the extract filtered. The filtrate was concentrated to a small volume and transferred to an alumina column. Elution with benzene/petroleum ether (1/6) afforded [Mo(η-C_5H_5)$(CO)_3I$] while elution with benzene/petroleum ether (1/3) gave a second red band which was collected. Removal of the solvent under reduced pressure and crystallisation of the resulting residue from benzene/petroleum ether gave [Mo(η-C_5H_5)$(CO)_2P(C_6H_5)_3I$] as a mixture of its *cis*- and *trans*-isomers. The residue from the filtration was dissolved in dichloromethane and the solution filtered. The filtrate was concentrated and yellow crystals of [Mo(η-C_5H_5)$(CO)_3P(C_6H_5)_3$][$B(C_6H_5)_4$] were obtained by addition of petroleum ether.

Synthesis of [Mo(η-C_5H_5)$(CO)_2py_2$][$B(C_6H_5)_4$]

A suspension of [{Mo(η-C_5H_5)$(CO)_3\}_2(\mu$-I)][$B(C_6H_5)_4$] (0.51 g, 0.5 mmol) in pyridine (ca. 20 ml) at 40°C was stirred for 30 min. The pyridine was removed under reduced pressure and the residue was extracted with benzene. The residue from this filtration was in turn extracted with dichloromethane and the extract filtered. Red crystals of [Mo(η-C_5H_5)$(CO)_2py_2$][$B(C_6H_5)_4$] were obtained from the filtrate by addition of petroleum ether. Yield: ca. 45%.

Synthesis of [Mo(η-C_5H_5)(CO)LX_3] (X = Br and Cl; L = $P(OCH_3)_3$, $P(CH_3)_2$-C_6H_5 and $P(C_2H_5)_3$) and [Mo(η-C_5H_5)(CO)$P(OCH_3)_3I_3$]

A solution of Cl_2 (1.0 mmol) in CCl_4 (ca. 10 ml) or Br_2 (0.16 g, 1.0 mmol) in CCl_4 (ca. 10 ml) or I_2 (0.25 g, 1.0 mmol) in benzene (ca. 30 ml) was added dropwise to a stirred solution of [Mo(η-C_5H_5)$(CO)_2LX$] (X = Br or Cl; L = $P(OCH_3)_3$, $P(CH_3)_2C_6H_5$ or $P(C_2H_5)_3$) (1.0 mmol) or [Mo(η-C_5H_5)$(CO)_2$-$P(OCH_3)_3I$] (0.47 g, 1.0 mmol) in benzene (ca. 50 ml). The precipitate which separated from solution was collected, washed with benzene and petroleum ether and dried thoroughly. Yield: ca. 60%.

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