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TRANSITION METAL COMPLEXES OF YLIDIC CYCLOPENTADIENYLIDES

I. TRIPHENYLPHOSPHONIUM CYCLOPENTADIENYLIDE AND RELATED LIGANDS*

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SUMMARY

Group VIA metal complexes of triphenylphosphonium cyclopentadienylide have been studied as internally stabilised analogues of cyclopentadienyl Group VIA metal tricarbonyl anions. The influence of intramolecular metal–phosphorus interaction on the reactivity of the metal centre has been examined. The complexes have been shown to be capable of coupling with diazonium ions, of being oxidatively halogenated and of forming stable adducts with Lewis acids. In each case the site of reaction is the metal atom. Reaction of the molybdenum complex with an amminium perchlorate salt causes oxidative dimerisation and formation of a Mo–Mo bond. The reaction of tetraphenyldiazocyclopentadiene with di-iron nonacarbonyl has been shown to lead to formation of the corresponding (tetraphenylcyclopentadienyl)iron dicarbonyl dimer.

INTRODUCTION

Some years ago Wilkinson and co-workers[1] synthesised a series of zwitterionic complexes (Ia–c) from the Group VIA metal hexacarbonyls and the ylidic ligand triphenylphosphonium cyclopentadienylide[2]. Complexes (Ia–c) are closely related to the well-known cyclopentadienyl Group VIA metal tricarbonyl anions. However, the considerable stability of complexes (Ia–c) contrasts sharply with the reactivity of the parent anionic carbonyl complexes. Following the Dahl–Ballhausen–Green[3] interpretation of the bonding in π-cyclopentadienyl metal tricarbonyls, Kotz and Pedrotty[4] have pointed out that a reasonable picture of the bonding in complexes (Ia–c) involves the presence of three filled non-bonding orbitals on the metal nucleus. However, these authors did not allude to the interesting problem raised by the increased stability of (Ia–c) vis-à-vis their anionic analogues. It seems reasonable to us that this stability is attained by reduction of excess electron density on the metal

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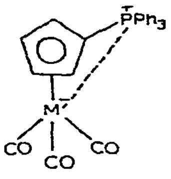
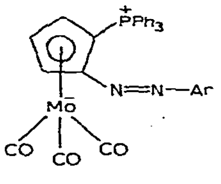
* Some of this work has already been reported in communication form[25]. The word "nucleophiles" in the title of this communication is in error and should read "electrophiles".

nucleus via interaction of one of the filled metal non-bonding orbitals with a vacant *d* orbital at the phosphonium centre. Carbonium[5] and phosphonium[6] centres α to a metal-complexed cyclopentadienyl ring are known to interact strongly with the metal atom, either directly or via the cyclopentadienyl ring. It seemed worthwhile to study the chemistry of complexes (Ia–c) and similar systems in order to determine the extent to which such interaction modifies the chemistry of the related anionic species. When most of our work had been completed Kotz and co-workers[4,7] published the results of a parallel study. Fortunately, there was little duplication of research effort.



(Ia), M = Cr
(Ib), M = Mo
(Ic), M = W



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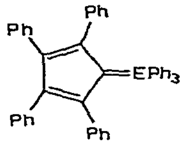
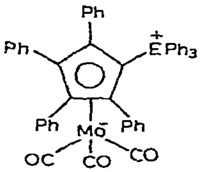


(IIIa), E = P
(IIIb), E = As
(IIIc), E = Sb



(IVa), E = P
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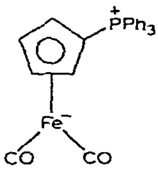
(IVc), E = Sb



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RESULTS AND DISCUSSION

Complexes (Ia) and (Ib) were prepared as described by Wilkinson[1], by the reaction of the appropriate hexacarbonyl with the ligand in boiling diglyme. Like Kotz and Pedrotty[4] we were unable to prepare the tungsten complex (Ic) in this manner and used instead the more reactive tris(acetonitrile)tungsten tricarbonyl[8] as precursor. The purple arylazosubstituted molybdenum complex (II, Ar = p-$CH_3OC_6H_4$–) was also prepared by this latter route. This proved to be very unstable and decomposed on recrystallisation. The instability of compound (II) could be interpreted as indicating interaction of lone-pair electrons on the azo group with the adjacent phosphonium centre[2b]. This in turn would depress metal–phosphorus interaction and destabilise the complex. However, the carbonyl stretching frequencies of this complex occur at higher wave-number than in complex (Ib) (Table 1) indicating increased electron withdrawal from the molybdenum centre compared to the latter complex. Other factors, therefore, must be responsible for the instability of complex (II).

A series of substituted analogues of triphenylphosphonium cyclopentadienylide (IIIa–c) were available[9] containing phosphorus, arsenic and antimony at the positively charged centre. In these ligands the degree of ring–heteroatom *p–d* bonding decreases

TABLE 1

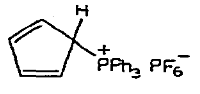
INFRA-RED ABSORPTIONS AND MELTING POINT DATA FOR VARIOUS GROUP VIA METAL COMPLEXES

No.	M.p.(°C)	ν(CO) (cm^{-1})	ν(N=N) (cm^{-1})
(II)	[a]	1924(s), 1830(s), 1819(ssh)[b]	
(IVa)	234	1920(s), 1813(s)[c]	
(IVb)	188–190	1919(s), 1814(s)[c]	
(VIIa)	193–195	1997(s), 1925(s)[b]	1589(msh), 1581(m)[b]
(VIIb)	193–196	1993(s), 1909(s)[b]	1584(msh), 1586(m)[b]
(VIIc)	168–170	1993(s), 1926(s)[b]	1584(msh), 1575(m)[b]
(VIII)		1892(s)[b]	1540(s)[b]
(IXa)	214–215	2064(s), 2005(s), 1976(s)[b]	
(IXb)	193–195	2063(s), 2008(s), 1982(s)[b]	
(IXc)	184–185	2052(s), 1997(s), 1976(s)[b]	
(X)	180	2033(s), 1993(s), 1964(s)[b]	
(XIVc)		2058(w), 2027(m), 1981(s), 1930(s)[b]	
(XVIII)	205–206	2037(vw), 1988(s), 1947(m), 1791(s)[b]	

[a] Not determined, complex decomposes; see text. [b] In KBr disc. [c] In methylene chloride solution. (s) = strong, (m) = medium, (sh) = shoulder.

in the order P > As > Sb[9]. We attempted the synthesis of the tricarbonylmolybdenum complexes of these ligands also. It was envisaged that any difference in the ability of the heteronium centres to accept electron density from the metal nucleus would be readily reflected in the position of the carbonyl stretching vibrations in the resulting complexes. Complexes (IVa) and (IVb) were easily prepared via tris(acetonitrile)-molybdenum tricarbonyl[8]. However, all attempts to synthesise the antimony analogue (IVc) yielded only uncharacterisable carbonyl-containing products. Complexes (IVa) and (IVb) both show two strong carbonyl absorptions at almost identical wave-numbers in methylene chloride solution (Table 1). Arsenic and phosphorus would, therefore, seem to be equally capable of functioning as electron sinks in these complexes. An attempt was also made to synthesise the zwitterionic iron complex (V) by the reaction of triphenylphosphonium cyclopentadienylide with iron pentacarbonyl in boiling dimethoxyethane. The unreacted ligand was recovered in 65% yield. Chromatography of the reaction products yielded traces of a yellow crystalline iron carbonyl complex. This material showed four carbonyl absorbtions in the region 1900–2100 cm^{-1} and is therefore evidently not complex (V). Insufficient quantities of the complex were isolated for further characterisation.

King has shown that cyclopentadienylmolybdenum tricarbonyl anion reacts with aryldiazonium salts to give stable neutral cyclopentadienylmolybdenum arylazo dicarbonyl complexes[10]. King failed to prepare the related tungsten complex[10] which was subsequently isolated by Nesmeyanov *et al.*[11]. Aryldiazonium ions are very poor electrophiles and seemed to us, therefore, to be useful reagents with which to probe the degree of residual negative charge on the metal atom in carbonyls (Ia–c). All three complexes (Ia–c) and the related (tetraphenylcyclopentadienyl)-molybdenum complex (IVa) reacted instantaneously with *p*-anisyldiazonium hexafluorophosphate in methylene chloride at room temperature. Under these conditions the chromium complex (Ia) underwent complete decomposition. The only charac-



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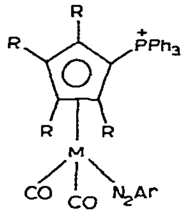
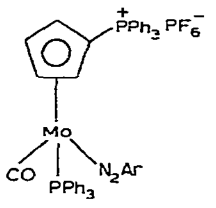


(VIIa), R = H, M = Mo
(VIIb), R = H, M = W
(VIIc), R = Ph, M = Mo

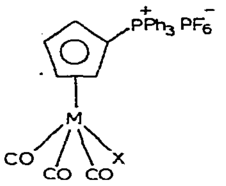


(VIII)

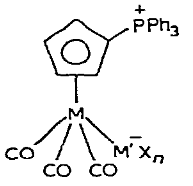
terisable product was the conjugate acid of the ylidic ligand, isolated as the hexafluorophosphate salt (VI). The products from the reactions with complexes (Ib), (Ic) and (IVa) were the corresponding {[arylazo)dicarbonylmetal]cyclopentadienylidenyl}triphenylphosphonium hexafluorophosphates, (VIIa–c). Complexes (VIIa) and (VIIb) are stable highly crystalline scarlet solids. Complex (VIIc) is light-brown in colour. The yield in all three reactions was greater than 90%. The fact that complexes (Ia–c) and (IVa) react rapidly and quantitatively with such a poorly electrophilic reagent indicates that—despite metal–phosphorus interaction—there is still a significant degree of residual negative charge on the metal nucleus. The absence of any detectable amounts of σ-phenyl complexes[11] in the products of these reactions (produced presumably via a redox reaction between diazonium ion and complex followed by a free radical arylation process) reflects the low sensitivity of complexes (Ib), (Ic) and (IVa) to oxidation.

Reaction of cyclopentadienylmolybdenum[10] or -tungsten[11] (arylazo)dicarbonyl with triphenylphosphine[10] or triphenyl phosphite[11] results in replacement of one carbonyl group in the azo complex. Similarly, complex (VIIa), when refluxed for six hours with triphenylphosphine in THF, gave the red, poorly crystalline monocarbonyl complex (VIII). Replacement of a carbonyl group by the relatively poorly π-accepting triphenylphosphine ligand results in increased electron release from the metal atom to the remaining ligands. Consequently the carbonyl and azo[12] stretching frequencies in compound (VIII) occur at lower wave-number than in the unsubstituted analogue (VIIa) (see Table 1). Complex (VIII) has an asymmetric pseudo-tetrahedral molybdenum centre and is capable of existing in two optically isomeric forms. Attempts to resolve complex (VIII) and some related arylazo complexes are currently under way.

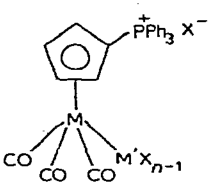
The reactions of complexes (Ia–c) with halogens and halogenating agents was also investigated. Treatment of the chromium complex (Ia) with one equivalent of bromine in methylene chloride at −70° gave a deep-red solution which turned green on warming to −25°. The only characterisable product from this reaction, after work-up with aqueous ammonium hexafluorophosphate, was the protonated ligand salt (VI). The red solutions obtained in a similar fashion from the molybdenum complex (Ib) on treatment with chlorine, bromine or iodine were stable at room temperature. Concentration of the solutions yielded red carbonyl-containing solids, soluble in aqueous ethanol, from which they could be precipitated as hexafluorophosphate salts. The colour of the highly crystalline salts varied from light-orange (chlorine) through salmon-pink (bromine) to dark-red (iodine). The iodination product (IXc), analysed correctly for [(iodotricarbonylmolybdenum)cyclopentadienylidenyl]triphenylphosphonium hexafluorophosphate. The chlorination and bromination products (IXa) and (IXb) could be readily purified to the point where their infra-red spectra was unchanged by further recrystallisation. However meaningful analytical data could not be obtained for these salts, possibly due to the presence of overhalogenated[13] ionic products. All these complexes showed three strong carbonyl bands in their infra-red spectra (see Table 1) and the remainder of the spectra were quite similar. To minimise the possibility of overhalogenation, we examined the reactions of (Ib) with milder halogenating reagents. Kotz and Pedrotty have shown that solutions of (Ib) in trifluoroacetic acid form [(hydridotricarbonylmolybdenum)cyclopentadienylidenyl]triphenylphosphonium trifluoroacetate[4]. Cyclopentadienylmolybdenumhydridotricarbonyl is known to react with carbon tetrachloride to yield cyclopentadienylmolybdenumchlorotricarbonyl[14]. It was not surprising, therefore, to find that addition of a THF solution of carbon tetrachloride or carbon tetrabromide to a solution of complex (Ib) in trifluoroacetic acid yielded deep red solutions, from which, after concentration and work-up with aqueous ethanolic ammonium hexafluorophosphate, the halotricarbonyl complexes (IXa) and (IXb) could be isolated in 80–90% yield. Complexes (IXa) and (IXb) prepared by this route could be recrystallised to analytical purity and had infra-red spectra identical to those of the products of direct halogenation. Treatment of a solution of the tungsten complex (Ic) in trifluoroacetic acid with carbon tetrabromide gave, after work-up, a complex which is believed to be [(bromotricarbonyltungsten)cyclopentadienylidenyl]triphenylphosphoniumhexafluorophosphate (X). The infra-red spectrum of complex (X) was very similar to that of the corresponding molybdenum complex (IXb). Completely satisfactory analytical data could not be obtained for this complex although the results were in general agreement with the assigned structure. Antimony pentachloride in methylene chloride has had some use as a mild reagent for the oxidative chlorination of arene[15] or cyclopentadienyl[16]-metal tricarbonyls. Complex (Ib) reacted smoothly with this reagent to give the chlorotricarbonyl (IXa) in good yield. The initial product from the direct halogenation of complex (Ib) with bromine is presumably the bromide (or tribromide) salt analagous to complex (IXb). This reacted with sodium borohydride in aqueous ethanol to regenerate complex (Ib) in quantitative yield thus ruling out the marginal possibility of ring halogenation in the interaction of complex (Ib) with halogens.



(IXa), M = Mo, X = Cl
(IXb), M = Mo, X = Br
(IXc), M = Mo, X = I
(X), M = W, X = Br



(XI)



(XI')

In the course of their study[4,7] of complexes (Ia–c) Kotz and co-workers have shown that all three complexes form stable 1/1 adducts with the strong Lewis acid boron trifluoride[4]. The basic site in complexes (Ia–c) was shown to be the metal atom, as would be predicted on the basis of the Dahl–Ballhausen Green formulation[3,4] of these complexes. Surprisingly, the 1/1 adduct formed between complex (Ib) and trimethylaluminium[7] involves a co-ordinate bond from one of the carbonyl oxygen atoms to the aluminium atom. More recently, Burlitch and Petersen[17] have noted a directly analogous variation in the site of complexation for the adducts formed between cyclopentadienyltungsten tricarbonyl anion and the triphenyls of indium and aluminium respectively. We were initially encouraged to investigate the Lewis base properties of complex (Ib) by a report that arenemolybdenum tricarbonyl complexes, isoelectronic with (Ib), form both 1/1 and 1/2 adducts with mercuric chloride[18]. Reaction of complex (Ib) with a variety of metal halide Lewis acid species resulted in the formation of several new Lewis acid–base adducts (XIa–f) (Table 2). The complexes are white or yellow crystalline solids, moderately air-stable but light-sensitive. All complexes except (XIe) and (XIg) analysed correctly for 1/1 adducts. No evidence for the formation of 1/2 adducts was found although excess Lewis acid was generally used in the preparation of the adducts. The gallium tribromide adduct (XIe) could not be separated from traces of the parent complex (Ib). This adduct was identified on the basis of its infra-red spectrum which is very similar to that of the other adducts but showed low-intensity carbonyl absorptions characteristic of complex (Ib). The tungsten complex (Ic) forms an adduct with mercuric chloride for which satisfactory analytical data could not be obtained. However, the structure (XIg) was assigned to this complex on the basis of the considerable similarity between its infra-red spectrum and that of the related molybdenum complex (XIb). Complex (XIh), an analogous 1/1 adduct of complex (Ic) and indium tribromide was also prepared. As would be expected the carbonyl absorptions of all the adducts lie at higher wave-number than in the parent tricarbonyls reflecting the reduced electron density at the donor metal site in the adduct. The carbonyl absorptions in our adducts also occur at much higher wave-number than in the adduct formed between cyclopentadienyltungsten tricarbonyl anion and triphenylindium[17]. Although the nature of the electron-pair acceptor will also affect the position of the carbonyl absorptions the determining factor in the latter case is likely to be the presence of a full formal negative charge at the donor site. The presence of strong carbonyl absorptions in the 2000–1870 cm^{-1} region and the absence of strong absorptions in the 1600 cm^{-1} region establishes that these adducts involve a direct metal–metal heteronuclear bond and are structurally analogous to the boron trifluoride adduct isolated by Kotz[4] and to Burlitch's triphenylindium complex[17].

TABLE 2

CARBONYL ABSORPTIONS[a] AND OTHER DATA FOR THE LEWIS ACID ADDUCTS OF COMPLEXES (Ib) AND (Ic)

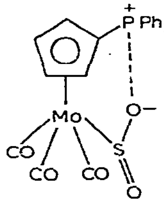
No.	M	$M'X_n$	M.p. (°C)	ν(CO) (cm^{-1})		
(XIa)	Mo	CdI_2	205	1975	1900	1870
(XIb)	Mo	$HgCl_2$	212–213	1979	1928	1889
(XIc)	Mo	$HgBr_2$	195	1979	1926	1891
(XId)	Mo	HgI_2		1994	1927	1903
(XIe)	Mo	$GaBr_3$	[b]	1997	1929	1903
(XIf)	Mo	$InBr_3$	200	1998	1928	1897
(XIg)	W	$HgCl_2$	198–200	2000	1930	1905
(XIh)	W	$InBr_3$		1999	1930	1890

[a] Potassium bromide disc. [b] Not determined; contains some (Ib) (see text).

Both neutral (XI) and ionic (XI′) formulations are possible for all the adducts synthesised. Unfortunately most of the compounds are too insoluble, even in polar solvents, for reliable conductivity measurements. However, the mercuric iodide complex (XId), which is reasonably soluble in acetone, had a molar conductance of 65 mho·cm^2·mole^{-1} for a 10^{-3} *M* solution. This value seems rather high for a neutral complex but is lower than that expected for a 1/1 electrolyte[19]. Attempts to convert the indium tribromide adduct (XIf) to a hexafluorophosphate salt by metathesis with ammonium hexafluorophosphate were not successful. No firm conclusions as to the nature of the adducts can therefore be arrived at. A similar ambiguity surrounds the structure of the mercuric halide adducts of the arenemolybdenum tricarbonyl complexes[18].

The yellow molybdenum tricarbonyl (Ib) gives intense blood-red solutions in liquid sulphur dioxide or in methylene chloride saturated with sulphur dioxide. These solutions slowly decompose on standing yielding amorphous brown carbonyl-free products. Rapid evaporation of freshly-prepared solutions gave a deep-red solid which quickly turned yellow. This yellow product proved to be unchanged complex (Ib). Thin-film infra-red spectra of the red solid could be obtained before decomposition was complete. Apart from strong peaks at 1920 and 1808 cm^{-1}, characteristic of complex (Ib) a medium-intensity peak at 2028 cm^{-1} and two strong peaks at 1988 and 1968 cm^{-1} were also found. From these results, it would seem that complex (Ib) reacts reversibly with sulphur dioxide to give a weakly bound adduct in which sulphur dioxide behaves as a Lewis acid[20]. The molybdenum sulphinate complex (XII) represents a plausible structure for this adduct.

From his work with complexes (Ia–c) Kotz[4] has concluded that they are "hard" bases. It was, therefore, of interest to determine whether complex (Ib) would displace carbon monoxide from cyclopentadienyldiiodocobalt carbonyl. The relatively high oxidation state of the cobalt atom in this complex renders it particularly sensitive to attack by "hard" bases. A dark red ionic complex was isolated from the reaction of complex (Ib) with the cobalt complex in hot methylene chloride. This could be readily converted into a hexafluorophosphate salt. Surprisingly, this material turned out to be [(iodotricarbonylmolybdenum)cyclopentadienylidenyl]triphenylphosphonium hexafluorophosphate (IXc). It is conceivable that the molybdenum–cobalt complex (XIII) is a precursor of complex (IXc) in this reaction.



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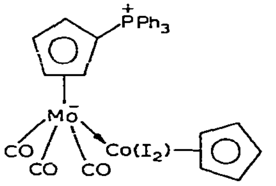
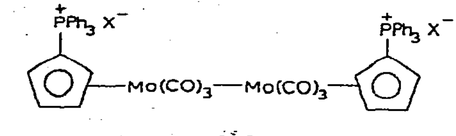
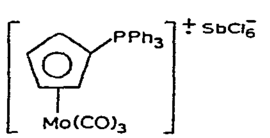


(XIII)

Since complexes (Ib) and (Ic) readily form adducts with Lewis acids it may be argued that stabilisation of the complexes via metal–phosphorus interaction is small compared to the strength of the metal–Lewis acid co-ordinate bond. However, adduct formation does not necessarily preclude metal–phosphorus interaction, although such interaction is no longer necessary to reduce excess electron density on the metal atom.

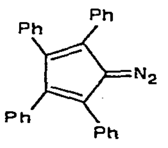


(XIVa), $X = SbCl_6$
(XIVb), $X = ClO_4$
(XIVc), $X = PF_6$



(XV)

Cyclopentadienylmolybdenum tricarbonyl anion, as has been mentioned before, is very sensitive to oxidation. It was, therefore, of interest to examine the reactions of the internally stabilised (Ib) with oxidising agents. Organoamminium radical-cations have been proposed as clean powerful one-electron oxidants[21]. Complex (Ib) reacted instantaneously with tris(*p*-bromophenyl)amminium hexachloroantimonate[21] in methylene chloride solution. The product, however, was a [(chlorotricarbonylmolybdenum)cyclopentadienylidenyl]triphenylphosphonium salt which was readily converted into the corresponding hexafluorophosphate (IXa). The expected dimeric complex (XIVa) was not isolated. Use of the corresponding amminium perchlorate[21] however, did yield the dimer as the purple perchlorate salt (XIVb). Due to the explosive nature of complex (XIVb) microanalytical data could not be obtained. Neither, because of its insolubility in hydroxylic solvents, could (XIVb) be converted into a more stable salt. A purple cationic molybdenum complex had earlier been isolated in low yield from abortive attempts to nitrosate complex (Ib) with nitrosonium hexafluorophosphate. The infra-red spectrum of this material was identical to that of complex (XIVb), allowing for the difference in anion. Analytical data for this stable complex was in agreement with structure (XIVc). The infra-red data, therefore, support our conclusion that the product from the reaction of complex (Ib) and the organoamminium perchlorate is complex (XIVb). Further confirmation of this structure for the perchlorate salt was provided by the facile regeneration of complex (Ib) when (XIVb) was treated with sodium borohydride. In the formation of (XIVc) the nitrosonium ion is evidently behaving as a one-electron oxidant. Formation of complex (IXa) from (Ib) via the ammonium hexachloroantimonate may proceed via initial formation of the complex radical-cation (XV). Halide-radical transfer from anion to cation would account for the isolation of complex (IXa).



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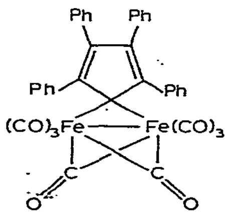
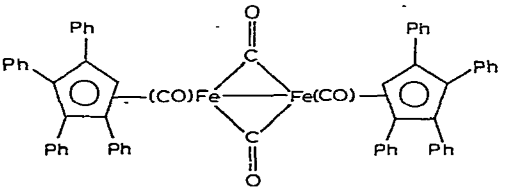


(XVII)



(XVIII)

Some preliminary experiments have been carried out to probe the ligand capability of the ylidic diazotetraphenylcyclopentadiene (XVI)[22]. Decomposition of compound (XVI) is known to yield tetraphenylcyclopentadienylidene[23]. It was hoped to synthesise carbene complexes of type (XVII) via the decomposition of diazo compound (XVI) in the presence of diiron nonacarbonyl. Reaction of compound (XVI) with diiron nonacarbonyl in benzene or THF at 40° gave a black-purple complex in 20% yield. The infra-red spectrum of this material (Table 1) had absorptions in the regions characteristic of terminal and bridging carbonyl groups. Microanalytical data showed the complex to be bis(tetraphenylcyclopentadienyl)tetracarbonyldiiron (XVIII). Attempts by previous workers to synthesise compound (XVIII) had not been successful[24]. Currently we are proceeding with some experiments designed to discover whether the metal–phosphorous interaction in complexes (Ia–c) operates via a direct orbital overlap or through the ring system. The chemistry of analogues of (Ia–c) with other than Group VB elements at the heteronium centre is also being probed.

EXPERIMENTAL

Metal carbonyls, phosphines, arsines, dicyclopentadiene and other basic reagents were available commercially and were used as received. Tetrahydrofuran was dried by distillation from lithium aluminium hydride under nitrogen. Acetonitrile and methylene chloride solvents were dried over molecular sieve. Melting points were determined on an Electrothermal melting-point apparatus and are not corrected. Where melting points are not given the complexes decomposed slowly above 200°. Infra-red spectra were recorded on a Perkin–Elmer 257 spectrometer. Microanalyses were by the Pascher Microanalytical Laboratory, 54 Buchstrasse, 53 Bonn, W. Germany and by Miss Dolores Healy of this Department.

[(Tricarbonylmetal)cyclopentadienylene]triphenylphosphoranes (Ia–c) and ring-substituted phosphorane and arsenane analogues (II), (IVa) and (IVb)

The chromium, molybdenum and tungsten complexes (Ia–c) were prepared as described by Kotz and Pedrotty[4] except that chromatographic treatment was not found necessary for the tungsten complex (Ic). The procedure used for the preparation of [(tricarbonylmolybdenum)(*p*-methoxyphenylazo)cyclopentadienylene]triphenylphosphorane (II), [(tricarbonylmolybdenum)tetraphenylcyclopentadienylene]-triphenylphosphorane (IVa) and -arsenane (IVb) was essentially that described by the above authors for complex (Ic) except that boiling THF was used as the reaction medium. Yields were 60% (II), 88% (IVa) and 73% (IVb). These complexes were purified by recrystallisation from methylene chloride/petroleum. During recrystallisation complex (II) decomposed and only the parent ligand triphenylphosphonium (*p*-methoxyphenylazo)cyclopentadienide was recovered.

Compound (Ia): (Found: C, 67.89; H, 4.43; P, 6.33. $C_{26}H_{19}CrO_3P$ calcd.: C, 67.53; H, 4.14; P, 6.69%.)

Compound (Ib): (Found: C, 61.37; H, 3.65; Mo, 19.60; P, 5.86. $C_{26}H_{19}MoO_3P$ calcd.: C, 61.66; H, 3.78; Mo, 19.14; P, 6.11%.)

Compound (Ic): (Found: C, 52.51; H, 3.27; P, 5.57. $C_{26}H_{19}O_3PW$ calcd.: C, 52.55; H, 3.22; P, 5.21%.)

Compound (IVa): (Found: C, 73.86; H, 4.32; Mo, 12.35; P, 4.08. $C_{50}H_{35}MoO_3P$ calcd.: C, 74.08; H, 4.38; Mo, 11.83; P, 3.82%.)

Compound (IVb): (Found: C, 70.75; H, 4.33; As, 8.93; Mo, 11.38. $C_{50}H_{35}AsMoO_3P$ calcd.: C, 70.27; H, 4.13; As, 8.76; Mo, 11.23%.)

Reaction of p-anisyldiazonium hexafluorophosphate with complexes (Ib), (Ic) and (IVa)

Provision of a nitrogen atmosphere was not necessary for these reactions. A stirred solution of the appropriate complex in methylene chloride was treated, at room temperature over a period of 2 min with one equivalent of solid diazonium hexafluorophosphate. Gas was evolved and the initially yellow solution became intensely red. Slow addition of ether to the filtered solution precipitated the crystalline arylazo complexes (VIIa–c) in better than 90% yield. Analytically pure samples were obtained by repeated precipitation with ether from methylene chloride solutions.

Complex (VIIa): (Found: C, 50.78; H, 3.62; Mo, 12.92; N, 3.77; P, 9.13. $C_{32}H_{26}F_6MoN_2O_3P_2$ calcd.: C, 50.68; H, 3.46; Mo, 12.65; N, 3.70; P, 8.17%.)

Complex (VIIb): (Found: C, 45.20; H, 3.13; N, 3.36; P, 7.18; W, 21.25. $C_{32}H_{26}F_6N_2O_3P_2W$ calcd.: C, 45.42; H, 3.10; N, 3.32; P, 7.34; W, 21.74%.)

Complex (VIIc): (Found: C, 63.3; H, 4.25; Mo, 8.97; N, 2.65; P, 5.95. $C_{56}H_{42}F_6MoN_2O_3P_2$ calcd.: C, 63.30; H, 3.39; Mo, 9.35; N, 2.64; P, 5.83%.)

Reaction of {[(p-methoxyphenylazo)dicarbonylmolybdenum]cyclopentadienylidenyl}-triphenylphosphonium hexafluorophosphate (VIIa) with triphenylphosphine

The molybdenum complex (VIIa), (0.5 g) was refluxed under nitrogen with 3 equivalents of triphenylphosphine in ca. 15 ml THF until disappearance of the carbonyl absorption at 1997 cm^{-1} (see Table 1) indicated that reaction was complete (ca. 6 h). Solvent was removed *in vacuo* and the light-red solid residue (VIII) was recrystallised from methylene chloride/ether. (Found: C, 59.08; H, 4.15; Mo, 9.98; N, 3.36. $C_{49}H_{41}F_6MoN_2O_2P_3$ calcd.: C, 59.29; H, 4.17; Mo, 9.67; N, 2.83%.)

Reaction of the complexes (Ia–c) with halogens and halogenating reagents

(*a*). *Halogens.* A solution of the appropriate complex in methylene chloride was treated under nitrogen with a brief stream of chlorine [Complex (Ib)] or one equivalent of bromine [Complexes (Ia) and (Ib)] or iodine [Complex (Ib)] in the same solvent. The reaction of bromine with complex (Ia) was carried out at −70°. On allowing the reaction mixture to warm to −25° the originally red solution turned green. Solvent was removed at room temperature and the residue extracted with water. Addition of aqueous ammonium hexafluorophosphate to the aqueous extract precipitated cyclopentadienyltriphenylphosphonium hexafluorophosphate (XI). Yield 51%. (Found: C, 58.94; H, 4.30. $C_{23}H_{20}F_6P_2$ calcd.: C, 58.50; H, 4.27%.)

All halogenations of compound (Ib) were carried out at room temperature. Removal of solvent from the reaction mixture following iodination of complex (Ib) gave a red solid which was dissolved in water containing ca. 20% ethanol. Addition of excess aqueous ammonium hexafluorophosphate, followed by dilution with a large volume of water precipitated the hexafluorophosphate salt (IXc) which was recrystallised from methylene chloride/ether. Yield 93%. (Found: C, 40.46; H, 2.63; I, 16.69; Mo, 12.90; P, 7.97. $C_{26}H_{19}F_6IMoO_3P_2$ calcd.: C, 40.13; H, 2.47; I, 16.31; Mo, 12.34; P, 7.96%.)

The products of the direct chlorination and bromination of compound (Ib), isolated by work-up as described above for the iodination reaction, could not be obtained analytically pure (see text).

(*b*). *Trifluoroacetic acid/carbon tetrahalides.* The complex (ca. 0.5 g) was dissolved in trifluoroacetic acid (~5 ml) under nitrogen and a solution of excess carbon tetrachloride [Complex (Ib)] or carbon tetrabromide [Complexes (Ib) or (Ic)] in THF was added. The deep red solution was stirred for ca. 10 min, filtered, and the solvent removed *in vacuo*. The residue was extracted with water containing ca. 10% ethanol and the hexafluorophosphate salts (IXa), (IXb) and (X) precipitated with aqueous ammonium hexafluorophosphate. The complexes were recrystallised from methylene chloride/ether. Yields were 85% (IXa), 90% (IXb) and 67% (X). All three complexes were stable *in vacuo* but decomposed slowly in the air.

Complex (IXa): (Found: C, 45.99; H, 2.77; Cl, 5.37; F, 16.46; Mo, 13.77. $C_{26}H_{19}ClF_6MoO_3P_2$ calcd.: C, 45.48; H, 2.80; Cl, 5.17; F, 16.62; Mo, 13.99%.)

Complex (IXb): (Found: C, 43.12; H, 2.59; Br, 11.41; F, 15.98; Mo, 13.69; P, 8.01. $C_{26}H_{19}BrF_6MoO_3P_2$ calcd.: C, 42.71; H, 2.62; Br, 10.94; F, 15.60; Mo, 13.13; P, 8.49%.)

Complex (X) (see text): (Found: C, 40.72; H, 2.44; Br, 10.15; P, 7.24; W, 22.92. $C_{26}H_{19}BrF_6O_3P_2W$ calcd.: C, 38.13; H, 2.34; Br, 9.76; P, 7.58; W, 22.48%.)

(*c*). *Antimony pentachloride.* A stirred solution of 0.506 g of complex (Ib) in methylene chloride was treated under nitrogen with 0.598 g (2 equivs.) of antimony pentachloride in the same solvent. Addition of light petroleum precipitated the crude oily hexachloroantimonate salt which was converted to the corresponding hexafluorophosphate salt (IXa) as described in (*a*) above. Complex (IXa) prepared by this route was identical to that prepared as under (*a*) or (*b*) above.

Reaction of [(bromotricarbonylmolybdenum)cyclopentadienylidenyl]triphenylphosphonium hexafluorophosphate (IXb) with sodium borohydride

Complex (Ib) (1.1 g) was treated with bromine as described above. The crude bromotricarbonyl salt was dissolved in 150 ml of 60% aqueous ethanol and treated with ca. 5 equivs. of sodium borohydride in aqueous solution. Gas was evolved and a yellow solid precipitated from the reaction mixture. The precipitate was filtered off and dried *in vacuo*. This material was identified by its infra-red spectrum as complex (Ib). Yield 0.98 g (89%).

Lewis-acid adducts of complexes (Ib) and (Ic)

Solutions of complex (Ib) and (Ic) in methylene chloride were treated with ca. 2 equivs. of cadmium iodide (in THF), mercuric chloride or bromide (in ether), mercuric iodide (in methanol), gallium trichloride or indium tribromide (in THF). Reactions employing indium and gallium halides were carried out in a nitrogen-filled glove-box. The adducts, (XIa) [(Ib) + CdI_2, white], (XIb) [(Ib) + $HgCl_2$, yellow], (XIc) [(Ib) + $HgBr_2$, yellow], (XId) [(Ib) + HgI_2, yellow], (XIe) [(Ib) + $GaBr_3$, white], (XIf) [(Ib) + $InBr_3$, white], (XIg) [(Ic) + $HgCl_2$, yellow] and (XIh) [(Ic) + $InBr_3$, white] were precipitated by the addition of ether. Spectroscopic data for (XIa–h) are collected in Table 2. The insoluble complexes (XIa–c) and (XIh) were analysed as precipitated. Complexes (XId), (XIf) and (XIg) were recrystallised, with some difficulty, from methylene chloride/ether. Complex (XIe) could not be obtained completely free of (Ib) and was identified spectroscopically (see text). Yields of all adducts were ca. 70%.

Complex (XIa): (Found: C, 35.20; H, 2.14; I, 29.5; P, 4.04. $C_{26}H_{19}CdI_2MoO_3P$ calcd.: C, 35.80; H, 2.29; I, 29.09; P, 3.56%.)

Compound (XIb): (Found: C, 39.64; H, 2.56; Cl, 9.70; P, 3.28. $C_{26}H_{19}Cl_2HgMoO_3P$ calcd.; C, 40.15; H, 2.47; Cl, 9.12; P, 3.95%.)

Compound (XIc): (Found: C, 36.25; H, 2.40; P, 4.23. $C_{26}H_{19}Br_2HgMoO_3P$ calcd.: C, 36.01; H, 2.21; P, 3.58%.)

Compound (XId): (Found: C, 32.33; H, 2.14; P, 3.51. $C_{26}H_{19}HgI_2MoO_3P$ calcd.: C, 32.51; H, 1.99; P, 3.22%.)

Compound (XIf): (Found: C, 36.60; H, 2.17; Br, 28.3; Mo, 10.75; P, 3.60. $C_{26}H_{19}Br_3InMoO_3P$ calcd.: C, 36.28; H, 2.23; Br, 27.85; Mo, 11.16; P, 3.61%.)

Compound (XIg) (see text): (Found: C, 30.9; H, 2.07; Cl, 5.07; P, 2.53; W, 21.25. $C_{26}H_{19}Cl_2HgO_3PW$ calcd.: C, 36.08; H, 2.21; Cl, 8.20; P, 3.58; W, 21.24%.)

Compound (XIh): (Found: C, 32.04; H, 2.07, Br, 24.12; In, 11.74; P, 3.87; W, 19.86. $C_{26}H_{19}Br_3InO_3PW$ calcd.: C, 32.92; H, 2.03; Br, 25.29; In, 12.10; P, 3.27; W, 19.40%.)

Reaction of [(tricarbonylmolybdenum)cyclopentadienylene]triphenylphosphorane, (Ib) with cyclopentadienyldiiodocobalt carbonyl

A solution of complex (Ib) in methylene chloride was added to a stirred solution of cyclopentadienyldiiodocobalt carbonyl and the solution was heated briefly to the boiling point. Gas evolution was observed. The solvent was removed *in vacuo* and the red residue was converted to the corresponding hexafluorophosphate salt as described for complex (XIc) above. The material obtained in this manner was identical in every respect to that prepared by direct iodination of complex (Ib) (see above).

Oxidation of complex (Ib) with organoamminium salts[21]

(*a*). *Hexachloroantimonate salt.* Solid tris(*p*-bromophenyl) amminium hexachloroantimonate (1.63 g) was added in one portion under nitrogen to a stirred solution of complex (Ib) in methylene chloride. The yellow solution became deep-red. Concentration of the solution *in vacuo* gave a light-orange solid which was recrystallised from methylene chloride/ether. Satisfactory analytical data could not be obtained for this material. However, it was readily converted to a hexafluorophosphate salt identical with complex (IXa).

(*b*). *Perchlorate salt.* The procedure was as described above for the hexachloroantimonate salt. Removal of the solvent yielded a purple solid (XIVb) which was recrystallised from methylene chloride/ether. *The dry perchlorate salt (XIVb) may explode when struck or scratched.*

Reaction of complex (Ia) with nitrosonium hexafluorophosphate

The complex (0.2 g) was dissolved in ca. 5 ml dry THF and 0.06 g nitrosonium salt added with stirring. After 30 min at room temperature, the solution was filtered to yield 0.06 g. of purple crystalline dimeric salt (XIVc) which was recrystallised from methylene chloride/ether. (Found: C, 48.11; H, 3.23. $C_{52}H_{38}F_{12}Mo_2O_6P_4$ calcd.: C, 47.95; H, 2.95%.)

Reaction of tetraphenyldiazocyclopentadiene (XVI) with diiron nonacarbonyl

The diazo compound (XVI) (1.09 g) was stirred in ca. 30 ml benzene or THF at 40° with 1–4 equivs. of diiron nonacarbonyl. Gas was evolved and the solution turned dark red. Unreacted carbonyl was removed by filtration and the solvent removed *in vacuo*. The oily brown residue was repeatedly extracted with boiling hexane. From the extracts 70% unreacted diazo compound was recovered. The petroleum-insoluble fraction, blackish-purple crystals of complex (XVIII), was recrystallised from methylene chloride/petroleum. (Found: C, 76.80; H, 4.59; Fe, 11.60. $C_{62}H_{42}Fe_2O_4$ calcd.: C, 77.36; H, 4.40; Fe, 11.60%.)

The yield of complex (XVIII) was not affected by the nature of the solvent or the ratio of reactants.

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