

Preliminary communication

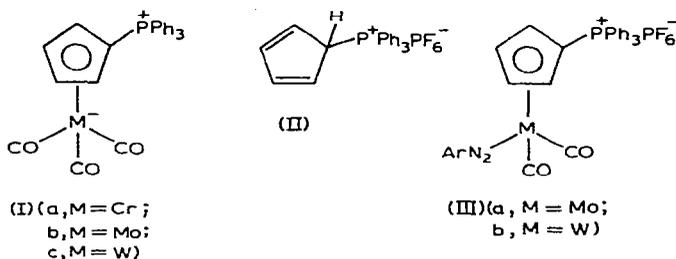
Reactions of various nucleophiles with the Group VIA metal tricarbonyl complexes of triphenylphosphonium cyclopentadienylide

D. CASHMAN and F.J. LALOR

Department of Chemistry, University College, Cork (Republic of Ireland)

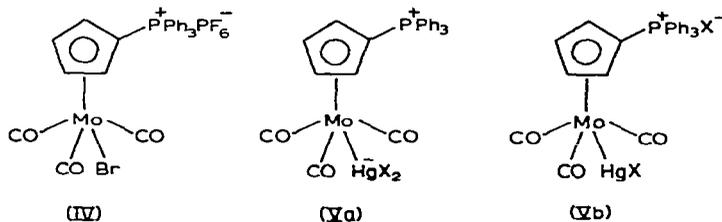
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Kotz and co-workers^{1,2} have recently demonstrated the Lewis-base character of the Group VIA metal tricarbonyl complexes (I)³ of triphenylphosphonium cyclopentadienylide⁴. When reacted with boron trifluoride or trifluoroacetic acid², the basic site in (I) is the metal atom, but trimethylalane forms an adduct in which the aluminium atom is bonded to one of the carbonyl oxygens¹. In these laboratories we have investigated the reactions of (I) with several other Lewis acids, among them the very weakly electrophilic *p*-anisyl diazonium ion.



All three complexes, (Ia–Ic) reacted readily with *p*-anisyl diazonium hexafluorophosphate in methylene chloride at room temperature. From the reaction with (Ia) only the fragmentation product (II) was isolated. However, both (Ib) and (Ic) gave the red, air-stable, arylazo complexes (IIIa) and (IIIb), in near-quantitative yield. No trace of *o*-aryl complexes could be detected⁵.

Both (Ia) and (Ib) reacted with one equivalent of bromine in methylene chloride at -70° . Complex (Ia) gave a deep red solution which turned green at -25° . After aqueous work-up, the only characterisable product was (II). Similar treatment of (Ib) gave a red cationic carbonyl complex (two strong bands at 2075 and 1990 cm^{-1} with a shoulder at 2070 cm^{-1}). Satisfactory analytical data could not be obtained for this material. The same product was formed when a solution of (Ib) in trifluoroacetic acid was treated with carbon tetrabromide in THF. We are, therefore, confident that this material is the bromo-tricarbonyl (IV).



Complex (Ib) reacted with mercuric chloride and bromide to give relatively air-stable, light sensitive 1/1 adducts. The mercuric chloride adduct could also be obtained, although in a less pure form, from the reaction of (Ib) with excess phenylmercuric chloride. Unlike the related arene molybdenum tricarbonyl complexes⁶, no trace of 1/2 adducts could be detected, even in the presence of excess mercuric halide. Both adducts show three strong carbonyl absorptions at ca. 1980, 1930 and 1895 cm^{-1} , but no strong absorption in the 1600 cm^{-1} region. The adducts therefore involve a Mo–Hg bond² but their insolubility makes it impossible to distinguish between the two possible structures, (Va) and (Vb).

The stability of (I), relative to the related cyclopentadienylmetal tricarbonyl anions, seems likely to depend on metal-to-phosphorus electron donation via *d*-orbital interaction. A similar interaction is thought to operate in some related systems⁷. Our work, and that of Kotz indicates that such interaction does not greatly depress the nucleophilic character of the metal atom.

Further studies on (I) and some related complexes are in progress, and will be reported at a later date.

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