Novel Routes to New Organoimido (Organonitrene) Complexes of Molybdenum, Rhenium, and Osmium

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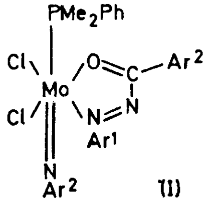
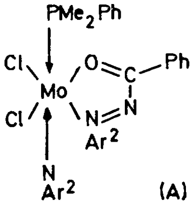
Summary The reaction of phosphinimines of the type $RN{=}PPh_3$ ($R = PhCO$ or Ph) with rhenium and osmium oxo-complexes provides a new route to arylimido-complexes and to the previously unknown rhenium aroylimido- and osmium arylimido-complexes; a series of novel molybdenum arylimido-derivatives has been obtained from a molybdenum oxo-complex and 1,2-disubstituted hydrazines.

Rhenium(v) phenylimido-complexes have previously been prepared by the reactions of $[ReCl_3O(PPh_3)_2]$ (**1**) with aniline,[1] phenyl isocyanate,[2] and 1-phenyl-2-benzoylhydrazine.[3] The Re=O bond in complex (**1**) resembles that of the carbonyl group in organic compounds in its reaction with aromatic amines, and we now report another parallel in its reaction with phosphinimines. Thus complex (**1**) reacts with $Ph_3P{=}NPh$ to give $[ReCl_3(NPh)(PPh_3)_2]$, paralleling the reaction of benzaldehyde to give $PhCH{=}NPh$. The less reactive benzoylphosphinimine $Ph_3P{=}NCOPh$ reacts analogously with (**1**) in refluxing toluene to give $[ReCl_3(NCOPh)(PPh_3)_2]$, which cannot be obtained from reaction of (**1**) with benzamide. This is a diamagnetic, air-stable blue crystalline solid with ν (C=O) in its i.r. spectrum at 1520 cm^{-1}. Attempts to replace the triphenylphosphine directly by more aliphatic phosphines (*cf.* ref. 1) led to loss of the NCOPh group.

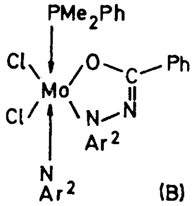


(I)

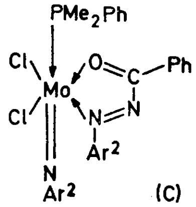
The reactions of the aroylphosphinimines $Ph_3P{=}NCOC_6H_4R$ ($R = H$, *p*-MeO, *p*-Cl) with $[OsOCl_3(PPh_3)_2]$[5] in refluxing xylene yield the corresponding arylimido-complexes $[Os(NC_6H_4R)Cl_3(PPh_3)_2]$ and not the aroylimido-derivative. These osmium arylimido-complexes are pink crystalline air-stable solids with magnetic moments of 2·2—3·3 B.M. and no bands in their i.r. spectrum assignable to ν (C=O). The arylimido-ligand may be derived from formation of the aroylnitrene radical [PhCON] and its subsequent rearrangement to PhNCO, which is known to give phenylimido-complexes with some transition metal oxo-complexes.[2]



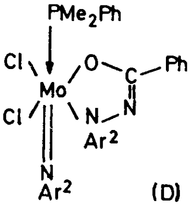
(A)



(B)



(C)



(D)

Phosphinimines do not react with $[MoOCl_2(PMe_2Ph)_3]$[6] even in refluxing xylene, but the 1-aryl-2-aroylhydrazines $Ar^1CONHNHAr^2$ ($Ar^1 = Ph$, $Ar^2 = Ph$, 1-naphthyl, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, or *p*-ClC_6H_4) react with the oxo-complex in refluxing methanol to give red, diamagnetic, crystalline molybdenum arylimido-complexes. Their analyses and i.r. and ^1H n.m r. spectra are consistent with the formulation $[MoCl_2(NAr^2)(ArCON_2Ar^2)(PMe_2Ph)]$ of structure (I), confirmed for the derivative $Ar^1 = Ph$, $Ar^2 = p\text{-}MeC_6H_4$ by *X*-ray analysis.[7] The complex with $Ar^2 = p\text{-}MeOC_6H_4$ has inequivalent *p*-MeO groups which appear in the ^1H n.m.r. spectrum as a doublet at τ6·22 and 6·29, the inequivalent methyl groups of the single dimethylphenylphosphine ligand giving rise to an adjacent pair of doublets centred at τ 8·22.

The above arylimido-complexes of rhenium(v) and osmium(v) may equally well be formulated as arylnitrene complexes of rhenium(iii) and osmium(iii) respectively. The molybdenum complexes may be formulated as arylnitrene derivatives of molybdenum(ii) (A), or (iv) (B) or arylimido-derivatives of molybdenum(iv) (D) or (vi) (D), which may be regarded as canonical forms of the true electronic structure.

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