

Preliminary communication

REVERSIBLE CARBON—CARBON BOND FORMATION BY INTERCONVERSION OF CO AND μ -ACYL LIGANDS ON THE FACE OF AN OSMIUM CLUSTER*

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Summary

Addition of PMe_2Ph to the μ -acyl complex

$(\text{O})\text{COs}_3\text{H}(\text{CO})_9 \{ \mu_3\text{-}\eta^2\text{-C}=\text{C}(\text{Ph})\text{C}=\text{C}(\text{Ph})\text{Re}(\text{CO})_4 \}$ (III) induces carbon—carbon bond cleavage with conversion of the μ -acyl group to a terminal CO ligand and gives the zwitterionic compound $[(\text{OC})_4\text{RePMe}_2\text{Ph}]^+ [\text{Os}_3\text{H}(\text{CO})_{10}\text{-}\{\mu\text{-C}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}\}]^-$ (IV).

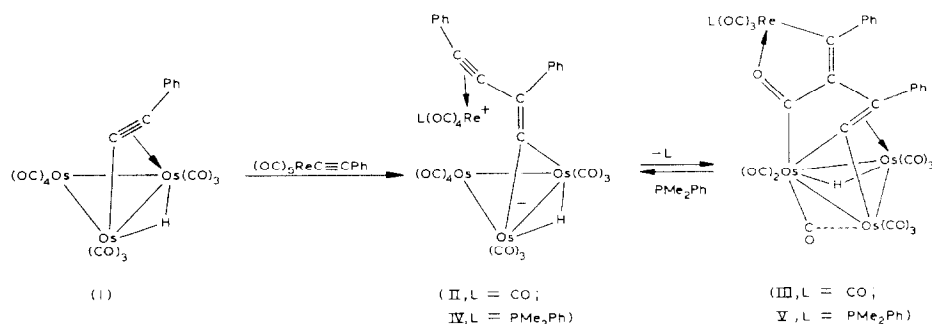
Facile elimination of CO (or PMe_2Ph) from IV at the rhenium atom leads to the back formation of a μ -acyl group and gives the complex $(\text{O})\text{COs}_3\text{H}(\text{CO})_9 \{ \mu_3\text{-}\eta^2\text{-C}=\text{C}(\text{Ph})\text{C}=\text{C}(\text{Ph})\text{Re}(\text{CO})_3\text{PMe}_2\text{Ph} \}$ (V) or complex III.

Recently we described the reaction of alkynes $(\text{OC})_5\text{MC}\equiv\text{CPh}$ ($\text{M} = \text{Mn}, \text{Re}$) with an osmium cluster $\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-}\eta^2\text{-C}\equiv\text{CPh})$ (I) under mild conditions, which gives the μ -acyl complexes $(\text{O})\text{COs}_3\text{H}(\text{CO})_9 \{ \mu_3\text{-}\eta^2\text{-C}=\text{C}(\text{Ph})\text{C}=\text{C}(\text{Ph})\text{M}(\text{CO})_4 \}$; the structure of the rhenium derivative III has been determined by an X-ray study [1].

The formation of III was proposed [2] to involve nucleophilic attack of alkyne at the "electrophilic" [3,4] β -carbon atom of the $\mu\text{-}\eta^2$ -acetylide ligand of the cluster I to give the intermediate zwitterionic compound II. (Complex I is fluxional owing to the oscillation of the $\text{C}\equiv\text{CPh}$ group between two osmium atoms [5], and it may suggest that in the transition state of this rearrangement the "carbocationic" character of the β -carbon atom is more pronounced [2]). Further steps include activation of the osmium carbonyl ligand toward carbon—carbon coupling by interaction of the carbonyl oxygen atom with rhenium, which is accompanied by substitution of the

*Dedicated to Professor Oleg Reutov on the occasion of his 65th birthday on September 5th, 1985.

CO ligand at the rhenium atom and migration of a rhenium carbonyl moiety to the carbon atom bearing a phenyl group (Scheme 1).



SCHEME 1

Compound II could not be obtained in an analytically pure state, because of gradual conversion of II to complex III but there is spectroscopic evidence for the formation of II as an intermediate.

We now have found good evidence for the intermediacy of zwitterionic compounds in the reaction of alkynes with cluster I. Treatment of III with PMe_2Ph induces cleavage of a μ -acyl carbon-carbon bond and gives a PMe_2Ph -substituted analog (IV, 80% yield) of II, which is a relatively more stable zwitterionic compound. Complex V ($\delta(^1\text{H}) - 19.57$ ppm, $\delta(^{31}\text{P}) - 14.93$ ppm) is another product isolated in modest yield ($\sim 15\%$) from the reaction mixture by TLC on silica gel.

Complex IV has been fully characterized by ^1H , ^{31}P and ^{13}C NMR studies and by elemental analysis. The ^1H NMR spectrum of IV in the hydride region shows a single resonance at $\delta -15.94$ ppm (CDCl_3 , 25°C), practically at the same position as the hydride resonance for II ($\delta -15.76$ ppm). The absence of splitting of the hydride resonance owing to ^1H - ^{31}P spin-spin coupling indicates that the phosphine ligand is not bound to any osmium atom of the Os_3 triangle. At the same time, the strong shielding of the phosphorus nucleus ($\delta -30.51$ ppm) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reveals that PMe_2Ph is bound to the rhenium atom rather than to a carbon atom of a hydrocarbon ligand.

Unambiguous evidence for carbon-carbon bond cleavage induced by the PMe_2Ph ligand was obtained from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the zwitterionic compound synthesized from the ^{13}C -labeled complex

$(\text{O})^{13}\text{COs}_3\text{H}(\text{CO})_9\{\mu_3-\eta^2-\text{C}=\text{C}(\text{Ph})\text{C}=\overset{\text{R}}{\text{C}}(\text{Ph})\text{Re}(\text{CO})_4\}$. The spectrum observed at -40°C (the complex is fluxional owing to "localized" carbonyl scrambling) contains ten resonances from terminal CO ligands at δ 170.83, 171.52, 172.09, 173.67, 174.93, 176.07, 178.41, 178.65, 178.73 and 180.11 ppm; the acyl resonance is not observed.

The strong shielding of the ^{31}P nucleus in the ^{31}P NMR spectrum of IV in comparison with that of V is consistent with localization of the positive charge on the rhenium atom in IV and relative deshielding of the osmium-CO ligand resonances in the ^{13}C NMR spectrum of IV is in accordance with localization of the negative charge on the Os_3 triangle.

The formation of complex V in the reaction of PMe_2Ph with III can be a result of direct CO substitution or of a stepwise sequence: $\text{III} \rightarrow \text{IV} \rightarrow \text{V}$. The latter possibility is confirmed by a separate experiment, upon heating in chloroform, CO and PMe_2Ph ligands are eliminated from IV to give V and III, respectively.

Thus, our observations illustrate the possibility of a direct attack of neutral carbon nucleophiles on a multisite-bound acetylide ligand of a cluster with formation of zwitterionic compounds. They also show the role of a carbonyl-oxygen-atom coordination with cationoid species in the activation of a CO ligand toward carbon-carbon bond formation.

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