Journal of Organometallic Chemistry, 250 (1983) C5—C8
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

METALLACYCLOBUTADIENE COMPLEXES FROM LIGAND COMBINATION OF CS AND ACETYLENE ON OSMIUM

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(Received November 9th, 1982)

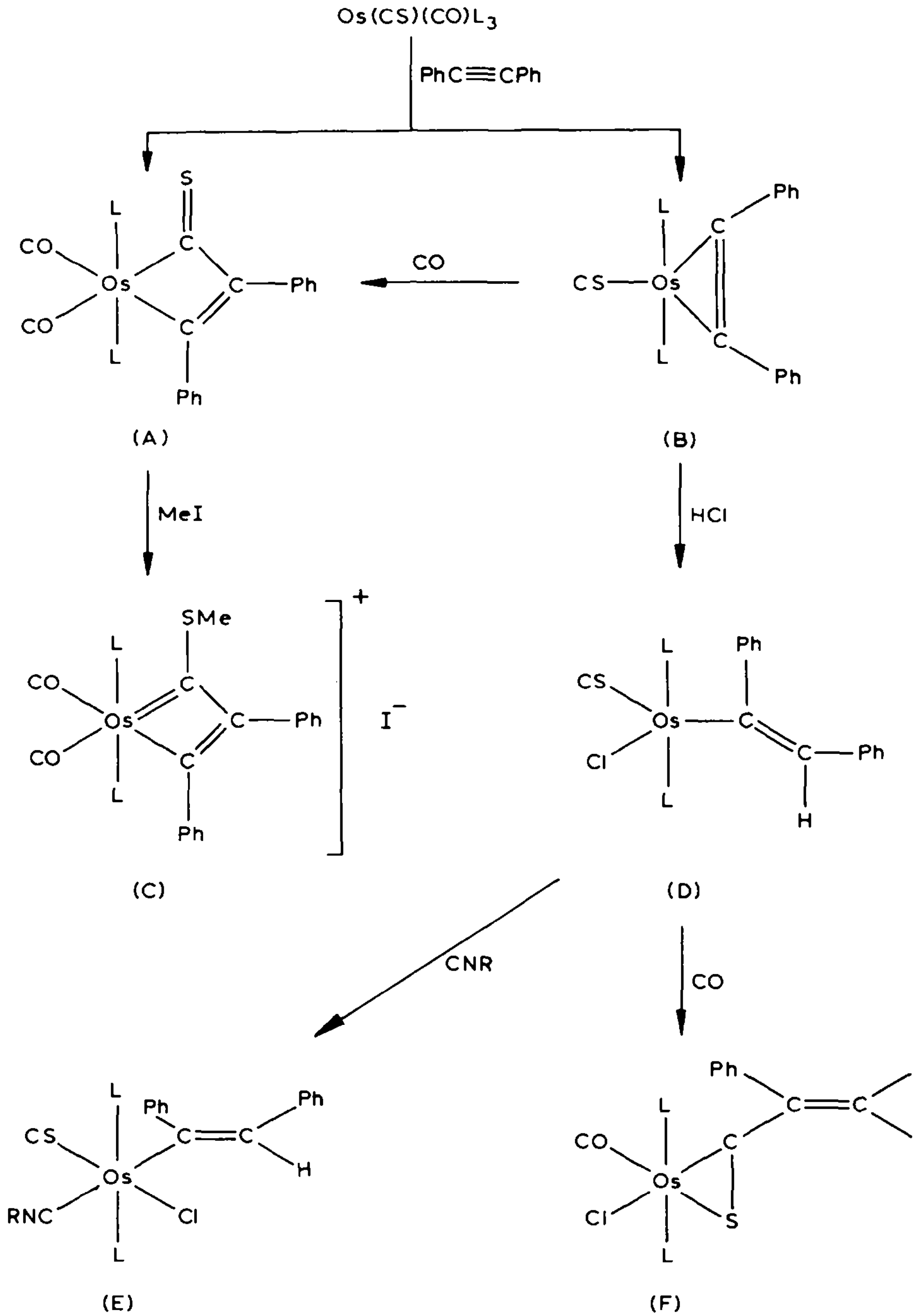
Summary

The zerovalent thiocarbonyl $\mathrm{Os(CS)(CO)(PPh_3)_3}$ reacts with the disubstituted acetylene $\mathrm{PhC{\equiv}CPh}$ to give an equal mixture of the metallacycle $\overline{\mathrm{Os(C[S]CPhC}}\mathrm{Ph)}$-$\mathrm{(CO)_2(PPh_3)_2}$ and the coordinatively unsaturated acetylene complex $\mathrm{Os(\eta^2\text{-}PhC{\equiv}CPh)(CS)(PPh_3)_2}$. Addition of CO converts the latter compound to the metallacycle which is readily alkylated on S to give, formally, a metallacyclobutadiene, e.g. $[\overline{\mathrm{Os(C\{SMe\}CPhC}}\mathrm{Ph)(CO)_2(PPh_3)_2}]^+$. HCl addition to $\mathrm{Os(\eta^2\text{-}PhC{\equiv}CPh)(CS)}$-$\mathrm{(PPh_3)_2}$ gives a coordinatively unsaturated *monohapto*-vinyl derivative $\mathrm{OsCl(\eta^1\text{-}CPh{=}CHPh)(CS)(PPh_3)_2}$. This complex adds CNR (R = *p*-tolyl) forming a six-coordinate complex $\mathrm{OsCl(\eta^1\text{-}CPh{=}CHPh)(CS)(CNR)(PPh_3)_2}$ but uptake of CO is accompanied by immediate rearrangement to the *dihapto*-thioacyl, $\mathrm{Os(\eta^2\text{-}C[S]\text{-}CPh{=}CHPh)Cl(CO)(PPh_3)_2}$.

Reaction between $\mathrm{Os(CS)(CO)(PPh_3)_3}$ and two molecules of ethyne gives $\overline{\mathrm{Os(\eta^2\text{-}C[S]CHCHCHC}}\mathrm{H)(CO)(PPh_3)_2}$, the first metallabenzene derivative [1]. We describe here the related reaction with disubstituted acetylenes which, interestingly, involves just one acetylene thus giving rise, after methylation at sulphur, to formal metallacyclobutadiene derivatives. This ring system has been postulated as an intermediate in the metathesis of acetylenes catalysed by transition metal carbyne complexes [2] and good support for this idea has come from isotopic labelling studies [3]. The results presented here provide further support for this mechanism in that a stable metallacyclobutadiene is characterised and furthermore the reaction forming this product can be considered as a direct interaction between a carbyne precursor (the CS ligand before *S*-alkylation) and an acetylene. A metallacyclobutadiene has been generated previously by the opening of a cyclopropenium cation at an iridium(I) centre [4].

As detailed in Scheme 1, reaction between $\mathrm{Os(CS)(CO)(PPh_3)_3}$ and $\mathrm{PhC_2Ph}$

0022-328X/83/$03.00



SCHEME 1. Synthesis of metallacyclobutadiene complexes of osmium and derivatives (L = PPh$_3$, R = *p*-tolyl).

proceeds in benzene under reflux over 20 min and the products are separated by chromatography on silica-gel with CH_2Cl_2 as eluant. Compound B (see Scheme 1) elutes first as an orange band yielding golden-orange crystals. Compound A follows as a second band and forms yellow-green crystals. CO at atmospheric pres-

TABLE 1

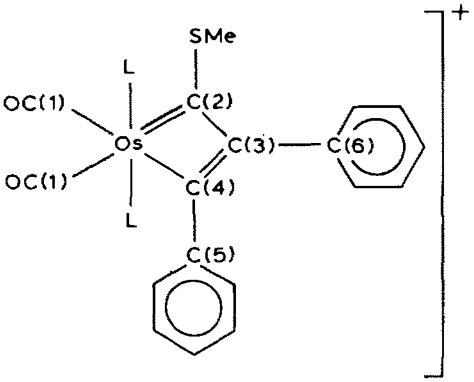
IR[a] DATA FOR NEW OSMIUM COMPLEXES

Compound[b]		ν(CO) (cm^{-1})	ν(CS) (cm^{-1})
$\overline{Os(C[S]CPhC}Ph)(CO)_2(PPh_3)_2$	(A)	1993, 1932	
$[\overline{Os(C[SMe]CPhC}Ph)(CO)_2(PPh_3)_2]I$	(C)	2020, 1960	
$Os(\eta^2\text{-}CPhCPh)(CS)(PPh_3)_2$	(B)		1250
$Os(\eta^1\text{-}CPhCHPh)Cl(CS)(PPh_3)_2$	(D)		1300
$Os(\eta^1\text{-}CPhCHPh)Cl(CS)(CNR)(PPh_3)_2$	(E)		1285
$Os(\eta^2\text{-}C[S]CPhCHPh)Cl(CO)(PPh_3)_2$	(F)	1900	

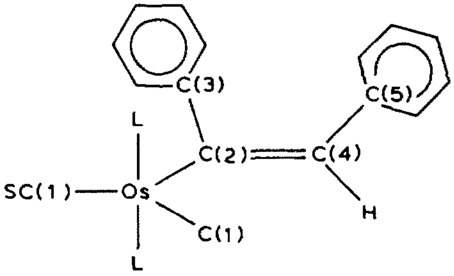
[a] Measured as Nujol mulls; all bands strong. [b] Satisfactory elemental analyses obtained for all compounds.

TABLE 2

^{13}C NMR DATA[a] FOR COMPOUNDS[b] C AND D



(C)



(D)

	(C)	(D)
δ(C(1))	184.19(t), 182.98(t)	261.80(t)
^2J(C—P)	8.5, 7.3	11.0
δ(C(2))	232.45(t)	146.28(t)
^2J(C—P)	9.7	6.1
δ(C(3))	166.91(t)	139.99(t)
^3J(C—P)	7.0	1.2
δ(C(4))	185.90(t)	123.72(s)
^1J(C—H)		37.1
^2J(C—P)	9.7	
δ(C(5))	137.12(t)	138.30(s)
^3J(C—P)	2.7	
δ(C(6))	139.72(s)	
δ(SMe)	25.04(s)	
^1J(C—H)	16.5	

[a] Measured in $CDCl_3$ at 24°C, chemical shifts in ppm downfield from Me_4Si, coupling constants in Hz. [b] L = PPh_3.

sure rapidly converts B into A. The sulphur atom of A is readily alkylated to afford cations, formal metallocyclobutadiene complexes, e.g. $[\overline{Os(C[SMe]CPhC}Ph)(CO)_2(PPh_3)_2]$ (C). IR data for the new compounds are presented in Table 1.

The ^{13}C NMR spectrum of compound C shows six resonances with phosphorus-coupling. These are assigned to the three metallacycle carbon atoms, the two carbonyl carbon atoms, and the *ipso*-carbon atom of the phenyl ring on the carbon atom adjacent to the metal centre. Details are presented in Table 2. An interesting feature is the strong phosphorus-coupling to C(3) of the ring, ${}^3J$(C—P) 7 Hz.

Compound B is a coordinatively unsaturated η^2-alkyne complex isoelectronic with Ir(η^2-PhC$_2$Ph)Cl(PPh$_3$)$_2$ [5]. Reaction of B with HCl affords the coordinatively unsaturated σ-alkenyl complex OsCl(η^1-CPh=CHPh)(CS)(PPh$_3$)$_3$ (D). A related molybdenum complex, Mo(η^2-CPh=CHPh)[P(OMe)$_3$]$_2$(η^5-C$_5$H$_5$) [6], has the ligand bound in a *dihapto*-arrangement. The possibility of a similar ring-closure for D was considered but the ^{13}C NMR spectrum (Table 2) excludes this possibility. The spectrum shows only two resonances with C—P coupling constants compatible with metal-bound carbon atoms, one from CS, the other from (η^1-CPh=CHPh). Immediate addition of CNR (R = *p*-tolyl) to D forms E indicating the unsaturated nature of D. A similar reaction with CO is accompanied by rapid rearrangement to an η^2-thioacyl complex (F), [7].

Acknowledgement. We thank Johnson-Matthey Ltd. for a generous loan of osmium tetroxide.

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