Novel Benzeneosmium Complexes containing Alkynyl, Vinyl, and Vinylidene Groups as Ligands
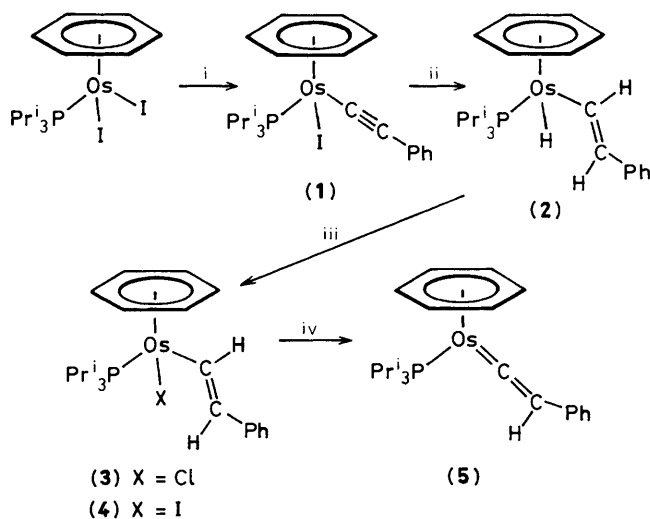
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The complex $C_6H_6Os(=C=CHPh)(PPr^i_3)$ has been prepared from $[C_6H_6OsI_2]_2$ *via* alkynyl(iodo)-, vinyl(hydrido)-, and vinyl(halogeno)-osmium compounds as precursors; it reacts with sulphur, selenium, and CuCl by electrophilic addition to the Os=C bond.

We have recently shown that vinylidenerhodium compounds $C_5H_5Rh(=C=CHR)(PPr^i_3)$ (R = H, Me, Ph)[1,2] are useful starting materials for the synthesis of half-sandwich type complexes containing vinyls,[3] allenes,[3] and thio-, seleno-, or telluro-ketenes as ligands.[4] In pursuing our general interest in metal-bases of the general type C_5H_5MLL' (M = Co, Rh, Ir) and C_6H_6MLL' (M = Ru, Os),[5] we attempted to prepare the benzenemetal analogues of the above-mentioned vinylidene-rhodium derivatives and study their reactivity, particularly towards electrophiles. For this purpose we required a new synthetic route to form the vinylidene unit, because the method developed for the cyclopentadienylrhodium complexes[1,2] could not be applied to the benzenemetal compounds.
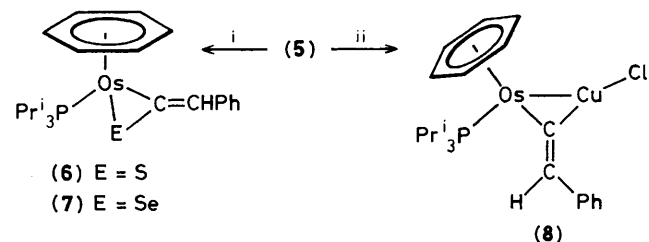
The four-step synthesis of $C_6H_6Os(=C=CHPh)(PPr^i_3)$ (5), which as far as we know is the first neutral vinylideneosmium half-sandwich complex,[6] is outlined in Scheme 1. The idea to use one of the 2-phenylethenylosmium compounds (3) and (4)

as a precursor was prompted by our recent finding that the (Z)-isomer of the rhodium complex $C_5H_5Rh(CH=CHPh)(PPr^i_3)Cl^2$ smoothly reacts with NEt_3 by elimination of HCl to produce the vinylidene compound $C_5H_5Rh(=C=CHPh)(PPr^i_3)$. The attempted preparation of (4) from $C_6H_6Os(PPr^i_3)I_2$[7] and $PhHC=CHLi$ or $PhHC=CHMgBr$ gave only minor amounts (2—5%) of the product which could not be separated in analytically pure form from other components.

The first step of the synthesis of (5), *i.e.*, the formation of (1)† by displacement of one halide ligand in $C_6H_6Os(PPr^i_3)I_2$ by the phenylacetylide anion, uses a method which has recently been described by Reger[8a] and Riera[8b] for the preparation of alkynyl-iron and -manganese compounds. There is no precedent, however, for the second step, *i.e.*, the formation of an hydrido(vinyl)metal complex from an alkynyl-(halide)metal precursor and $NaBH_4$ because such a reaction would be expected to give the alkynyl(hydrido) derivative. Compound (2)† is surprisingly stable and, in contrast to the rhodium analogue $C_5H_5RhH(CH=CHPh)(PPr^i_3)$, does not react on warming to form the styrene isomer

(1)

(2)

(3) X = Cl

(4) X = I

(5)

Scheme 1. *Reagents and yields:* i, PhC≡CH, AgPF₆, CH₂Cl₂, −78 °C, 70%; ii, NaBH₄, MeOH, 25 °C, 75%; iii, CCl₄, toluene, 0 °C, 98% (X = Cl), CH₂I₂, toluene, 35 °C, 95% (X = I); iv, Bu^{t}Li, Et₂O, −40 °C, 90%.

(6) E = S
(7) E = Se

(8)

Scheme 2. *Reagents:* i, S₈ or Se₈, C₆H₆, 25 °C; ii, CuCl, tetrahydrofuran, 40 °C.

$C_6H_6Os(CH_2=CHPh)(PPr^i_3)$.[2] The proposed (*E*)-configuration of the OsCH=CHPh unit in (2) is mainly supported by the large coupling constant (16.5 Hz) for the two =CH protons‡ which is expected to be much smaller for the (*Z*)-isomer.[9] We note that ethenyl(hydrido)-zirconium and -hafnium compounds $(C_5Me_5)_2MH(CH=CHR)$ (M = Zr, Hf) comparable in stability with (2) have very recently been prepared by Bercaw and coworkers on insertion of alk-1-ynes into one of the metal–hydride bonds of $(C_5Me_5)_2MH_2$.[10]

The crucial step in the synthesis of (5) is the abstraction of HX from the 2-phenylethenyl(halide) complexes (3) and (4)† which are formed in almost quantitative yield by hydride substitution of (2). Again the (*E*)-configuration is favoured (^1H n.m.r. data‡). In contrast to (*Z*)-C_5H_5Rh-(CH=CHPh)(PPr^i_3)Cl, (3) is completely inert to NEt_3 and even to $NaNH_2$, but reacts with Bu^{t}Li to produce the vinylideneosmium compound (5). The beginning of the elimination process is accompanied by a characteristic colour change from yellow *via* deep violet to brown. Destroying the excess of Bu^{t}Li with methanol at −78 °C, removal of the solvent, extraction of the residue with pentane, and column chromatography (basic Al_2O_3, activity grade V) gives the vinylidene complex (5)† the properties of which are similar to those of the rhodium analogue.[1] The most characteristic feature of the spectroscopic data‡ is the position of the signal of the vinylidene α-C atom in the ^{13}C n.m.r. spectrum which appears at δ 278.3, *i.e.* in the same region as for other M(=C=CHR) compounds.[6]

Compound (5) reacts with sulphur and selenium (Scheme 2) to give the intensely coloured chalcogenoketeneosmium compounds (6) and (7) in *ca.* 30% yield.†‡ The reaction is much slower than that of C_5H_5Rh(=C=CH$_2$)(PPr^i_3) with the same reagents and this is consistent with the frequently observed lower reactivity of 5d metal compounds compared with their 4d analogues.[11] As in the case of the vinylidenerhodium complexes,[4] the M=C rather than the C=C bond in (5) is the preferred site of attack for electrophiles. It is also possible to use (5) as a starting material for the synthesis of heterodinuclear complexes containing a bridging vinylidene ligand as is shown in the preparation of (8) which is formed in almost quantitative yield.

The novel route, shown in Scheme 1, for the formation of a vinylidene unit in the co-ordination sphere of a transition metal is possibly not restricted to the =C=CHPh ligand. Preliminary experiments indicate that the compounds analogous to (1)—(4), $C_6H_6Os(C\equiv CMe)(PPr^i_3)I$ and $C_6H_6Os-(CH=CHMe)(PPr^i_3)X$ (X = H, Cl, I), are formed under similar conditions to their phenyl counterparts. The final vinylidene complex $C_6H_6Os(=C=CHMe)(PPr^i_3)$, however, is apparently much less stable than the phenyl compound and could not be isolated.

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‡ *Selected spectroscopic data:* i.r. in KBr (ν in cm^{-1}); ^1H, ^{31}P, ^{13}C, n.m.r. (δ) in C_6D_6 at room temperature (*J* in Hz). (1) I.r., 2085 (C≡C). (2) I.r., 2065 (OsH), 1573 (C=C); ^1H n.m.r., 9.35 [1H, ddd, *J*(H$_α$–H$_β$) 16.5, *J*(H$_α$–H$_x$) 1.8, *J*(H$_α$–P) 5.0, H$_α$], 7.18 (6H, m, C_6H_5 + H$_β$), 4.76 [6H, d, *J*(H–H$_x$) 0.4, C_6H_6], −9.77 [1H, d, *J*(H$_x$–P) 40.0, H$_x$]; ^{31}P n.m.r. (off resonance), 27.4 [d, *J*(P–H) 25.3]; ^{13}C n.m.r., 131.72 [d, *J*(C$_α$–P) 15.4, C$_α$], 140.81 [d, *J*(C$_β$–P) 3.7, C$_β$]. (3) I.r., 1575 (C=C); ^1H n.m.r., 9.35 [1H, dd, *J*(H$_α$–H$_β$) 16.8, *J*(H$_α$–P) 2.6, H$_α$], 6.70 [1H, dd, *J*(H$_β$–H$_α$) 16.8, *J*(H$_β$–P) 2.4, H$_β$]; ^{13}C n.m.r., 141.07 [d, *J*(C$_α$–P) 18.4, C$_α$], 136.99 [d, *J*(C$_β$–P) 4.4, C$_β$]. (4) I.r., 1573 (C=C); ^1H n.m.r., 10.07 [1H, dd, *J*(H$_α$–H$_β$) 16.9, *J*(H$_α$–P) 3.2, H$_α$], 6.71 [1H, dd, *J*(H$_β$–H$_α$) 16.9, *J*(H$_β$–P) 2.2, H$_β$]. (5) I.r., 1568 (C=C); ^1H n.m.r., 3.14 [1H, d, *J*(H$_β$–P) 6.4, H$_β$], 4.88 (6H, s, C_6H_6); ^{13}C n.m.r., 278.30 [d, *J*(C$_α$–P) 22.2, C$_α$], 110.91 [d, *J*(C$_β$–P) 5.2, C$_β$]. (6) I.r., 1575 (C=C), ^1H n.m.r., 4.78 [1H, d, *J*(H$_β$–P) 4.0, H$_β$], 4.75 (6H, s, C_6H_6). (7) I.r., 1578 (C=C); ^1H n.m.r., 4.89 [1H, d, *J*(H$_β$–P) 4.8, H$_β$], 4.85 [6H, d, *J*(H–P) 0.2, C_6H_6]. (8) I.r., 1575 (C=C); ^1H n.m.r. (in CDCl$_3$), 5.64 [6H, d, *J*(H–P) 0.25, C_6H_6], 4.12 [1H, d, *J*(H$_β$–P) 5.8, H$_β$].