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Preliminary communication

REACTIONS OF TRANSITION METAL σ-ACETYLIDE COMPLEXES

III*. SYNTHESIS OF SOME ARYLDIAZOVINYLIDENE AND CYCLOHEPTATRIENYLVINYLIDENE COMPLEXES. X-RAY STRUCTURES OF $[Ru(C=CPhN=NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4] \cdot 0.67CH_2Cl_2$ AND $[Ru\{C=CPh(C_7H_7)\}(DPPE)(\eta\text{-}C_5H_5)][PF_6] \cdot 0.63CH_2Cl_2$

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Summary

Addition of arenediazonium or tropylium salts to $Ru(C_2Ph)(L)_2(\eta\text{-}C_5H_5)$ (L_2 = $(PPh_3)_2$ or DPPE) gives the corresponding cationic aryldiazovinylidene and cycloheptatrienylvinylidene complexes, respectively; the X-ray structures of the title complexes confirm the presence of the new ligands. The Ru—C and C=C distances are 1.823(9) and 1.34(1) Å for the aryldiazo complex, and 1.848(9) and 1.32(1) Å for the cycloheptatrienyl derivative.

The most commonly used methods for the synthesis of transition metal complexes containing vinylidene ligands are by direct reaction of 1-alkynes with a suitable metal substrate, or by protonation or alkylation of a metal acetylide complex [1]. Electrophilic addition to the β-carbon of the acetylide ligand has been extensively studied with reagents such as HBF_4 or HPF_6 [2], $[R_3O][BF_4]$ (R = Me or Et) or FSO_3Me [2, 3] and with alkyl halides [4]. Double addition of an electrophile has been reported in the successive reactions of $[W(C_2Bu^t)(CO)_5]^-$ with FSO_3Me or $[Et_3O]^+$ followed by CF_3SO_3H [5], and the addition of reactive metal hydrides to metal acetylides has given binuclear complexes with μ-vinylidene ligands [6].

Seeking to extend the range of known vinylidene ligands, we have studied the reactions of two classes of cationic organic reagents, arenediazonium and

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*For Part II, see ref. 12.

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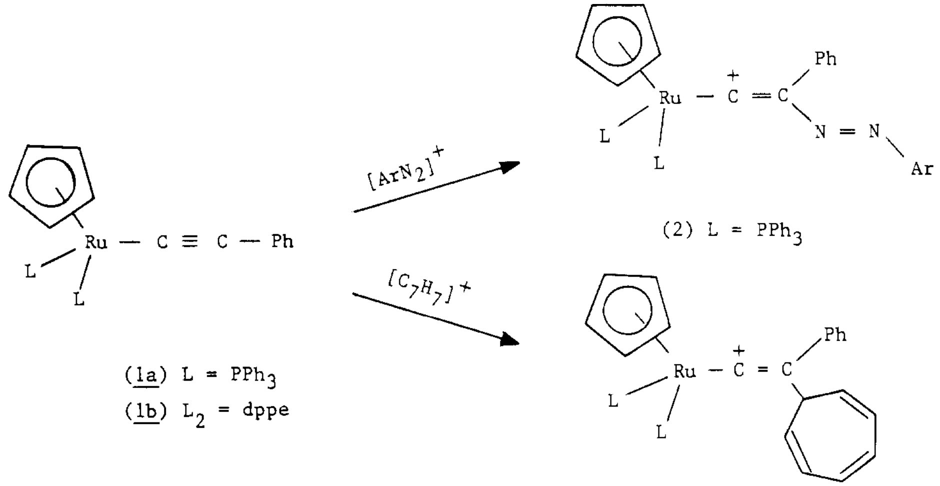
tropylium salts. Addition of $[ArN_2][BF_4]$ to solutions of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1a) in THF readily affords the corresponding aryldiazovinylidene complexes $[Ru(C{=}CPhN{=}NAr)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (2), which are isolated as bright red, air stable crystalline solids. The IR spectra contain bands at ca. 1550 cm^{-1} which can be assigned to $\nu(C{=}C) + \nu(N{=}N)$. In the NMR spectra, the expected resonances are found, with the characteristic low-field triplet (J(CP) 15.8 Hz) of the metal-bonded vinylidene α-carbon occurring at δ 362 ppm in the PhN_2 derivative. Similarly, the reaction between $Ru(C_2Ph)(DPPE)(\eta\text{-}C_5H_5)$ (1b) and $[C_7H_7][PF_6]$ gave $[Ru\{C{=}CPh(C_7H_7)\}(DPPE)(\eta\text{-}C_5H_5)][PF_6]$ (3) as a rose-pink powder. The ^1H NMR spectrum contains multiplets at δ 2.85, 5.34, 6.28 and 6.53 ppm (relative intensities 1/2/2/2), which are assigned to the protons attached to the C_7 ring, indicating the presence of a cycloheptatrienyl group; a triplet at δ 347 ppm in the ^{13}C NMR spectrum in the analogous PPh_3 complex confirmed their formulation as substituted vinylidene complexes.



(1a) L = PPh_3

(1b) L_2 = dppe

(2) L = PPh_3

(3) L_2 = dppe

Ar = Ph, $C_6H_3Me_2$-3,4, $C_6H_4NO_2$-4, $C_6H_3Cl_2$-2,4, C_6H_4OMe-4

We have fully characterised these novel ligands by single-crystal X-ray studies of the title complexes. Suitable crystals were grown from dichloromethane/methanol (2) and dichloromethane/ethanol mixtures (3). Diffraction data for both complexes were collected on an Enraf—Nonius CAD 4 four-circle diffractometer using graphite-monochromated Mo-K_α radiation, λ(Mo-K_α) 0.7107 Å.

Crystal data: $C_{57}H_{49}BF_4N_2P_2Ru \cdot 0.67CH_2Cl_2$ (2), M = 1069.33, monoclinic, space group $P2_1/n$; a 22.424(6), b 10.215(5), c 23.292(7) Å, β 104.64(2)°, U 5160 Å^3; D_m 1.37, D_c = 1.37 g cm^{-3} for Z = 4; $F(000)$ 2196 electrons, μ(Mo-K_α) 4.44 cm^{-1}. T = 293 K.

$C_{46}H_{41}F_6P_3Ru \cdot 0.63CH_2Cl_2$ (3), M = 955.4, triclinic, space group $P\bar{1}$; a 11.67(3), b 12.10(3), c 15.98(4) Å, α 76.6(2), β 88.3(1), γ 86.8(1)°, U 2191(8) Å^3; D_c 1.45 g cm^{-3} for Z = 2; $F(000)$ 972.9 electrons, μ(Mo-K_α) = 5.56 cm^{-1}. T = 293 K.

For 2, 4451 unique data (for 3, 3809) were collected in the range $1.2 < \theta < 21°$ ($1.3 < \theta < 21°$), of which 2847 (3432) with $I > 2.5\sigma(I)$ were refined to $R = 0.046$, $R_w = 0.049$ ($R = 0.059$, $R_w = 0.069$). Both structures were solved by obtaining the coordinates of the Ru atom from a Patterson map; all other non-hydrogen atoms were revealed in subsequent refinement and Fourier difference maps [7]. Neutral atom scattering factors were obtained from reference [8]. Both structures contain dichloromethane of crystallisation, the site occupancies of which were refined to 0.67 and 0.63 of a molecule for 2 and 3, respectively. The BF_4 anion in 2 was disordered, satisfactory refinement being obtained using a model with three orientations with site occupancies of 0.65, 0.25 and 0.10. For 2, all non-hydrogen atoms except phenyl group carbons and fluorines had anisotropic thermal parameters; for 3, only the phenyl carbons of the non-hydrogen atoms had isotropic thermal parameters. In the final cycles of the blocked-matrix least squares refinement, the phenyl and

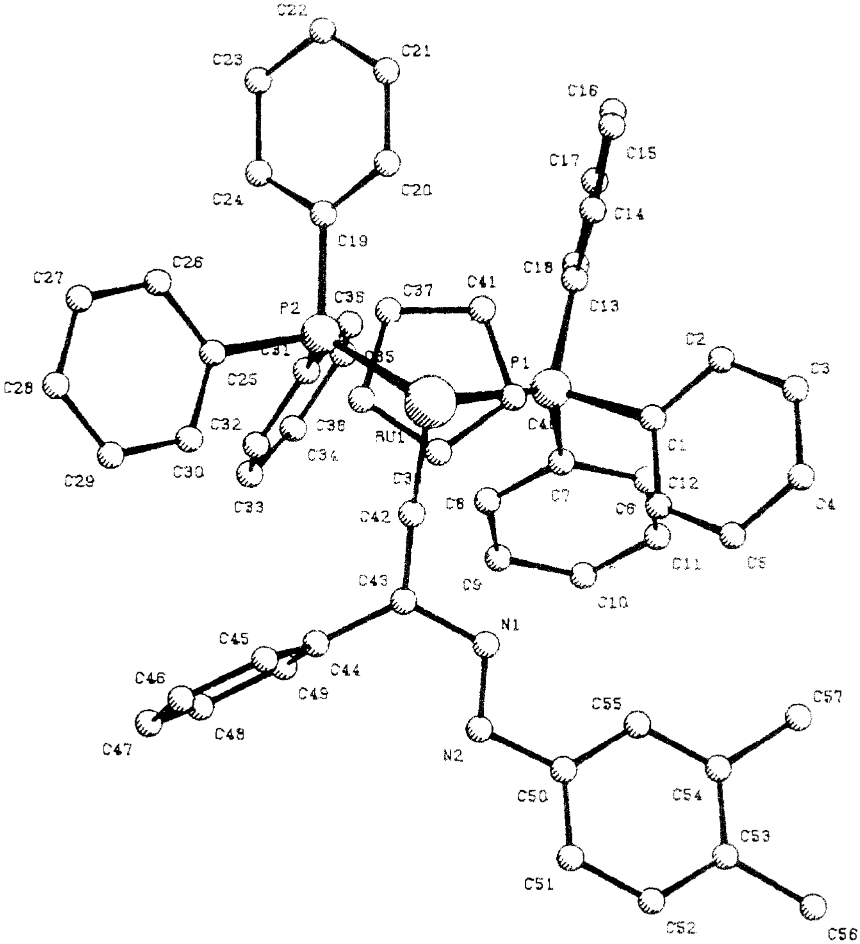


Fig. 1. PLUTO plot of cation in [Ru(C=CPhN=N$C_6H_3Me_2$-3,4)$(PPh_3)_2$(η-C_5H_5)] [BF_4] (2), showing atom numbering scheme. Bond distances: Ru(1)—C(cp) (av.) 2.28, Ru(1)—P(1) 2.362(3), Ru(1)—P(2) 2.360(3), Ru(1)—C(42) 1.823(9), C(42)—C(43) 1.34(1), C(43)—C(44) 1.48(1), C(43)—N(1) 1.42(1), N(1)—N(2) 1.27(1), N(2)—C(50) 1.42(1) Å; bond angles: P(1)—Ru(1)—P(2) 98.8(1), P(1)—Ru(1)—C(42) 96.1(3), P(2)—Ru(1)—C(42) 89.7(3), Ru(1)—C(42)—C(43) 169.9(7), C(42)—C(43)—C(44) 121.4(8), C(42)—C(43)—N(1) 114.4(8), C(43)—N(1)—N(2) 114.9(7), N(1)—N(2)—C(50) 113.0(7)°.

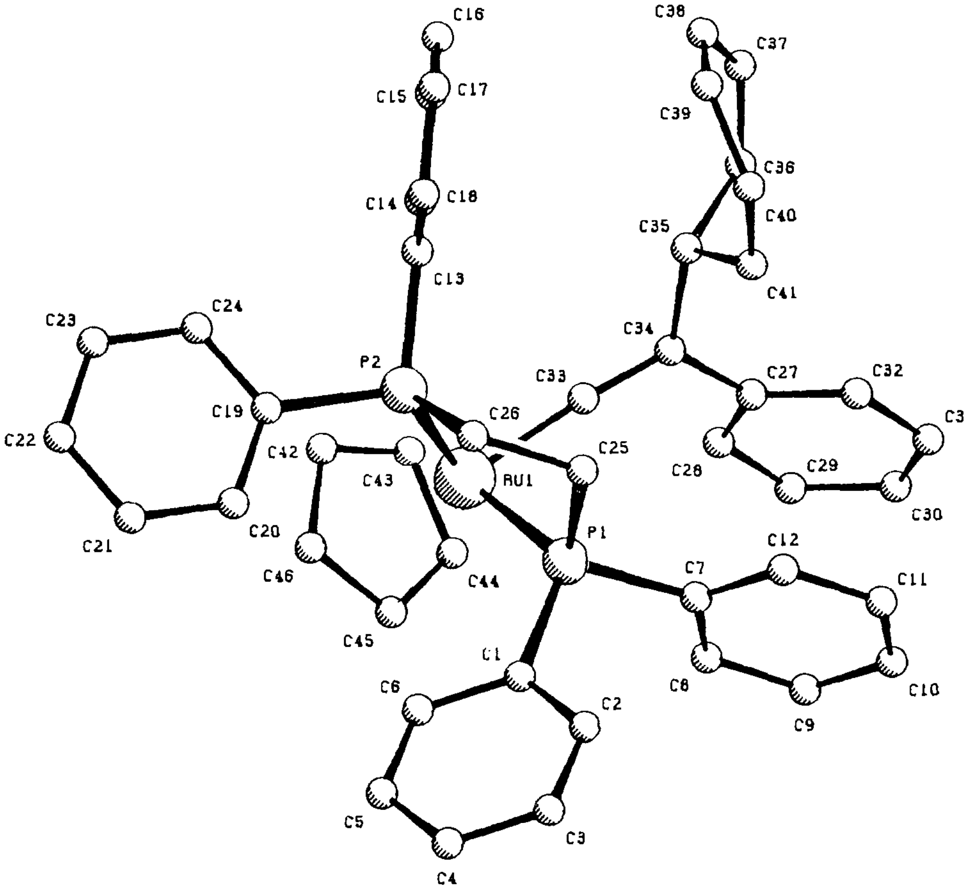


Fig. 2. PLUTO plot of cation in [Ru $\{C{=}CPh(C_7H_7)\}$(DPPE)(η-C_5H_5)] [PF_6] (3), showing atom numbering scheme. Bond distances: Ru(1)—C(cp) (av.) 2.26, Ru(1)—P(1) 2.298(2), Ru(1)—P(2) 2.305(2), Ru(1)—C(33) 1.848(9), C(33)—C(34) 1.32(1), C(34)—C(27) 1.483(9), C(34)—C(35) 1.55(1) Å; bond angles: P(1)—Ru(1)—P(2) 83.9(1), P(1)—Ru(1)—C(33) 81.6(2), P(2)—Ru(1)—C(33) 95.8(2), Ru(1)—C(33)—C(34) 174.9(6), C(33)—C(34)—C(27) 121.1(6), C(33)—C(34)—C(35) 118.1(7)°.

cyclopentadienyl rings were included as rigid groups (C—C 1.395 and 1.42 Å respectively) and the hydrogen atoms were placed in calculated positions (C—H 1.08 Å) with a common thermal parameter. The structures of the cations of 2 and 3 are illustrated in Figs. 1 and 2, respectively, which also give some selected bond distances and angles*.

Both cations are of the now familiar, nearly octahedral $RuLP_2(\eta$-$C_5H_5)$ structural type, and contain disubstituted vinylidene ligands. The Ru—C distances (1.823(9) Å in 2, 1.848(9) Å in 3) are considerably shorter than that expected for an Ru—C(*sp*) single bond; indeed, comparison with the Ru—CO distance recently determined [9] in [Ru(CO)($PPh_3)_2(\eta$-C_5H_5)] [BPh_4] indicates an even greater degree of backbonding from the metal into the vinylidene π^* orbitals. Both the Ru—C and the C=C distances of the vinylidene ligand

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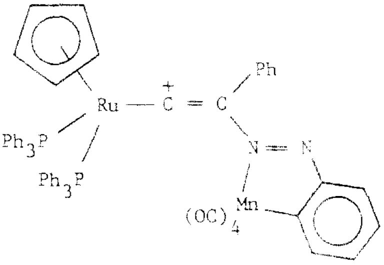
*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England). Any request should be accompanied by the full literature citation for this Communication.

(1.34(1) Å in 2, 1.32(1) Å in 3) are comparable with those found previously in $[Ru(C{=}CHMe)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (1.845(7) and 1.313(10) Å, respectively) [10]. The Ru—C—C system is nearly linear (RuC(42)C(43) 169.9(7)° in 2, RuC(33)C(34) 174.9(6)° in 3).

In 2, the phenyldiazo group adopts the usual *trans* configuration, the N—N and N—C parameters not differing significantly from those found for *trans*-azobenzene [11]. In 3, the C_7 ring has the tub conformation; of interest is the calculated location of the hydrogen atom attached to C(35), the C—H bond being directed towards the centre of a Ph group of the DPPE ligand.



(4)

The reactivity of these new complexes has been investigated briefly. Reaction with anionic nucleophiles (H^-, Me^-, OMe^-) results in displacement of the addend and regeneration of the neutral phenylacetylide complexes. The diazo function in 2 exhibits a remarkable tendency to bind to electrophiles such as H^+ or Me^+; the dicationic $[Ru(C{=}CPhNMe{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^{2+}$ and tricationic $[Ru(C{=}CPhNH{=}NHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^{3+}$ complexes resulting from such reactions have been identified so far. Not surprisingly, reacton with $MnMe(CO)_5$ affords the cyclometallated derivative 4. Full details of these and related complexes will be given elsewhere.

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