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Preliminary Communication

Reactions of novel cationic diphenylallenylidene complexes $[Ru(=C=C=CPh_2)L_2(\eta\text{-}C_9H_7)]^+$ ($L = PPh_3$; L_2 = bis(diphenylphosphino)methane, dppm or 1,2-bis(diphenylphosphino)ethane, dppe) with neutral and anionic nucleophiles

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Abstract

The synthesis of novel allenylideneruthenium(II) complexes $[Ru(=C=C=CPh_2)L_2(\eta\text{-}C_9H_7)]\,[PF_6]$ [$L = PPh_3$; L_2 = bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe)] is described. The allenylidene complexes are unreactive towards methanol but other nucleophiles [PMe_3, NaOMe, $LiC{\equiv}CR$ (R = Ph, n-C_3H_7)] can be added regioselectively to the C_γ atom to give alkynyl derivatives. $[Ru\{C{\equiv}C\text{–}CPh_2(PMe_3)\}(dppm)(\eta\text{-}C_9H_7)]\,[PF_6]$ isomerizes in tetrahydrofuran solution to the thermodynamically stable product $[Ru\{C(PMe_3)=C=CPh_2\}(dppm)(\eta\text{-}C_9H_7)]\,[PF_6]$.

Key words: Ruthenium; Allenylidene; Indenyl; Carbene; Alkynyl; Nucleophilic addition

Transition metal vinylidene complexes $[M]=C=CR_2$ have been widely studied in the last decade; but, the chemistry of the higher members of the metallacumulene series $[M]=C=(C)_x=CR_2$ ($x \geq 1$) is less well known [1]. There is increasing interest in this type of derivative and its use in chemical transformations mainly because of the unusual degree of unsaturation and as sources of the organic cumulenes $R_2C=(C)_x=CR_2$. The influence of the metal on the electronic distribution in the chain and the different ligand environments should modulate the reactivity of the cumulene system. MO calculations on the model $[Mn(=C=C=CH_2)(CO)_2(\eta\text{-}C_5H_5)]$ [2] showed that C_α and C_γ are electrophilic centres and that C_β is nucleophilic [3*]. However, the influence of the metal-containing moiety and the electronic influence of the ligands have yet to be investigated though previous results seem to imply dependence. Thus, allenylidene complexes $[Ru\{=C=C=C(R^1)R^2\}Cl(PR_3)(\eta\text{-arene})]^+$ add alcohols at C_α to give alkenylcarbene derivatives [4] whereas the cumulene ligand in complexes with isoelectronic fragments $[Ru(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ [5], $[RuCl(dppm)_2]^+$ [dppm = bis(diphenylphosphino)methane] [6] and $[RuCl(NP_3)]^+$ [$NP_3 = N(CH_2CH_2PPh_2)_3$] [7] is stable towards methanol or ethanol.

These results have prompted us to report our studies on the synthesis of novel allenylideneruthenium complexes with the metal-containing fragment $[RuL_2(\eta\text{-}C_9H_7)]^+$ (L_2=2PPh_3, dppm, dppe). We are interested to find out to what extent the electronic density on, and the steric properties of, this metal fragment affects the stabilization and the reactivity of the cumulene system as compared with $[Ru(PR_3)_2(\eta\text{-}C_5H_5)]^+$ and $[RuCl(PR_3)(\eta\text{-arene})]^+$. Here we describe the synthesis of the novel cationic propadienylidene complexes $[Ru(=C=C=CPh_2)L_2(\eta\text{-}C_9H_7)]^+$ (L_2 = 2PPh_3, dppm, dppe). We have also studied their reactivity towards typical nucleophiles such as alcohols, PMe_3, MeO^- and acetylide anions. The results are summarized in Scheme 1.

Complex $[RuCl(PPh_3)_2(\eta\text{-}C_9H_7)]$ reacts with two equivalents of 1,1-diphenyl-prop-2-yn-1-ol in refluxing methanol in the presence of $NaPF_6$ (in 1:2:2 molar ratio) for 15 min to give the violet allenylidene complex $[Ru(=C=C=CPh_2)(PPh_3)_2(\eta\text{-}C_9H_7)]\,[PF_6]$ (**1a**, 80%). The complex was chemically and spectroscopically characterized [8*]. The IR spectrum of **1a** shows typical $\nu(C=C=C)$ and $\nu(PF_6)$ absorptions at 1933 and 837 cm^{-1}, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **1a** in CD_2Cl_2 shows a single resonance at δ 47.92 ppm. The ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit the expected resonances for the indenyl and aromatic groups. The $^{13}C\{^1H\}$ NMR spectrum also shows signals at δ 290.90 (t, $^2J(P\text{-}C) = 18.6$ Hz), 208.44(s) and 156.59(s) ppm which may be assigned to the C_α, C_β and C_γ of the allenylidene.

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* Reference number with asterisk indicates a note in the list of references.

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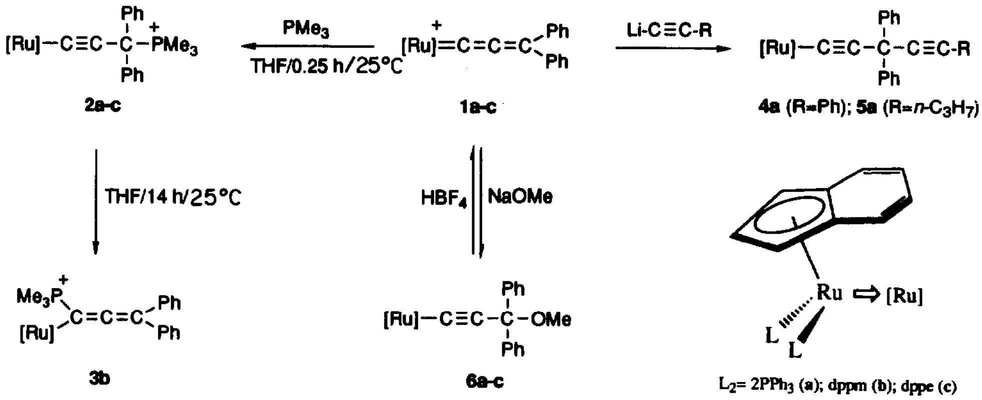

Scheme 1.

Similarly, we obtained $[Ru(=C=C=CPh_2)L_2(\eta\text{-}C_9H_7)][PF_6]$ (L_2 = dppm (**1b**), dppe (**1c**)) in high yields [8*].

The allenylidene complexes (**1a–1c**) do not add methanol and they were recovered unchanged from the methanol solutions after prolonged reflux; we also examined their reactivity towards other neutral and anionic nucleophiles (see Scheme 1). Thus, PMe_3 adds regioselectively to the C_γ atom yielding alkynyl derivatives (**2a–2c**). The IR spectra of **2a–2c** show the typical $\nu(C{\equiv}C)$ and $\nu(PF)$ absorptions and the $^{31}P\{^1H\}$ NMR spectra exhibit signals characteristic of the expected AX_2 system [**2a**: δ 30.25 (t, $^5J(P-P) = 4.1$ Hz, PMe_3), 52.57 (d, $^5J(P-P) = 4.1$ Hz, PPh_3) ppm. **2b**: δ 18.45 (d, $^5J(P-P) = 2.8$ Hz, dppm), 32.05 (t, $^5J(P-P) = 2.8$ Hz, PMe_3) ppm. **2c**: δ 32.14 (t, $^5J(P-P) = 3.9$ Hz, PMe_3), 88.51 (d, $^5J(P-P) = 3.9$ Hz, dppe) ppm] [8*]. Complex **2b** slowly rearranges in THF solution (14 h, room temperature) to give the alkenyl phosphonium ylide complex **3b** [8*]. The $^{31}P\{^1H\}$ NMR spectrum of **3b** also exhibits a signal characteristic of an AX_2 system δ 11.79 (d, $^3J(P-P) = 6.8$ Hz, dppm), 26.38 (t, $^3J(P-P) = 6.8$ Hz, PMe_3) ppm. The high values of the coupling constants are consistent with the addition of PMe_3 to the C_α atom of the allenylidene.

Regioselective additions to the C_γ of the allenylidene are also observed when anionic nucleophiles are used (see Scheme 1). Thus, complex **1a** reacts with $LiC{\equiv}CR$ (R=Ph or n-C_3H_7) at -20°C to furnish, after 15 min, a yellow solution from which alkynyl complexes (**4a**, **5a**) can be isolated [8*]. Similarly, when a THF solution of complexes **1a–1c** was treated with NaOMe for 30 min, yellow solids were isolated and identified from their NMR and IR spectra as methoxoalkynyl complexes [$L_2 = 2PPh_3$ (**6a**), dppm (**6b**), dppe (**6c**)] [8*]. The treatment of the alkynyl complexes **6a–6c** with HBF_4 or $MeOSO_2CF_3$ in diethyl ether does not lead to vinylidene complexes but regenerates the allenylidenes **1a–1c**.

Although a systematic study of the reactivity of allenylidene complexes has not yet been completed, the results reported here appear to suggest that the electrophilic character of **1a–1c** is less than that of $[Ru(=C=C=CPh_2)Cl(PR_3)(\eta\text{-arene})]^+$, probably due to the indenyl and phosphine ligands, since they are stable in MeOH and nucleophilic additions take place preferentially at C_γ. The isomerization observed in the nucleophilic addition with the relatively soft nucleophile PMe_3 suggests that this process is thermodynamically controlled. Further studies of the scope of the addition reactions to the cumulene system are in progress.

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3 $[Mn(=C=C=CR_2)(CO)_2(\eta\text{-}C_5H_5)]$ undergoes: (a) C_β additions of H^+ to give cationic vinylcarbyne complexes $[Mn({\equiv}CCH{=}CR_2)(CO)_2(\eta\text{-}C_5H_5)]^+$ (N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, O.M. Khitrova, A.S. Batsanov and Yu.T. Struchkov, *J. Organomet. Chem.*, *262* (1984) 39); (b) C_α additions of PPh_3 to give $[Mn\{C(PPh_3)C{=}CPh_2\}(CO)_2(\eta\text{-}C_5H_5)]$ (N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, O.M. Khitrova, A.S. Batsanov and Yu.T. Struchov, *J. Organomet. Chem.*, *265* (1984) 271), (c) $[Mn(=C=C=CPh_2)(CO)_2(\eta\text{-}C_5H_4CH_3)]$ undergoes C_γ additions of PPh_3 to give $[Mn(C{\equiv}C-C(PPh_3)Ph_2)(CO)_2(\eta\text{-}C_5H_4CH_3)]$ [2b].

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8 All new compounds isolated have been characterized by elemental analysis, mass spectra (FAB), conductance measurements, IR, ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. Key spectroscopic data are as follows. For **1a** (L_2=2PPh_3): IR (KBr) ν(C=C=C) 1933 and $\nu(PF_6)$ 837 cm^{-1}. ^{31}P{^{1}H} (CD_2Cl_2, 121.5 MHz): δ 47.92 (s) ppm. ^{1}H (CD_2Cl_2, 300 MHz): δ 5.00 (t, 1H, J = 2.5 Hz, Ind_5); 5.48 (d, 2H, J = 2.5 Hz, Ind_5); 6.61 (m, 2H, Ind_6); 7.00–7.73 (m, 42H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (CD_2Cl_2, 75.4 MHz): δ 87.20, 97.45, 112.40, 124.11 (Ind); 126.54–144.21 (Ph, Ind); 156.59, 208.44 (s, C_γ; s, C_β); 290.90 (t, ^2J(P–C) = 18.6 Hz, C_α) ppm. For **1b** (L_2 = dppm): IR (KBr) ν(C=C=C) 1935 and $\nu(PF_6)$ 838 cm^{-1}. ^{31}P{^{1}H} (CD_2Cl_2, 121.5 MHz): δ 8.18 (s) ppm. ^{1}H (CD_2Cl_2, 300 MHz): δ 4.45 (m, 1H, PCH_2); 5.34 (m, 1H, PCH_2); 5.61 (t, 1H, J = 2.8 Hz, Ind_5); 6.12 (d, 2H, J = 2.8 Hz, Ind_5); 6.99–7.62 (m, 34H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (CD_2Cl_2, 75.4 MHz): δ 48.85 (t, J(C–P) = 26.9 Hz, PCH_2); 80.16 (t, ^2J(C–P) = 1.8 Hz, Ind_5); 95.47, 111.72, 125.03 (Ind); 127.99–143.24 (Ph, Ind); 155.59, 202.25 (s, C_γ; s, C_β); 290.26 (m, C_α) ppm. For **1c** (L_2 = dppe): IR (KBr) ν(C=C=C) 1943 and $\nu(PF_6)$ 836 cm^{-1}. ^{31}P{^{1}H} (CD_2Cl_2, 121.5 MHz): δ 81.73 (s) ppm. ^{1}H (CD_2Cl_2, 300 MHz): δ 2.65 (m, 2H, $P(CH_2)_2$); 2.74 (m, 2H, $P(CH_2)_2$), 5.25 (t, 1H, J = 2.7 Hz, Ind_5); 5.72 (d, 2H, J = 2.7 Hz, Ind_5); 6.8–7.5 (m, 34H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (CD_2Cl_2, 75.4 MHz): δ 28.99 (m, $P(CH_2)_2$); 81.33, 97.07, 111.29, 124.60 (Ind); 126.48–143.32 (Ph, Ind); 157.32, 203.54 (s, C_γ; s, C_β); 292.84 (t, ^2J(P–C) = 19.2 Hz, C_α) ppm.

For **2a**: IR (KBr) ν(C≡C) 2041 and $\nu(PF_6)$ 840 cm^{-1}. ^{31}P{^{1}H} (CD_2Cl_2, 121.5 MHz): δ 30.25 (t, ^5J(P–P) = 4.1 Hz, PMe_3), 52.57 (d, ^5J(P–P) = 4.1 Hz, PPh_3) ppm. ^{1}H (CD_2Cl_2, 300 MHz): δ 1.76 (d, 9H, ^2J(H–P) = 12.6 Hz, PMe_3); 4.55 (d, 2H, J = 2.1 Hz, Ind_5); 5.02 (t, 1H, J = 2.1 Hz, Ind_5); 6.56 (m, 2H, Ind_6); 6.94–7.38 (m, 42H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (CD_2Cl_2, 75.4 MHz): δ 7.97 (d, J(C–P) = 53.8 Hz, PMe_3); 53.24 (d, J(C–P) = 54 Hz, C_γ); 72.66, 94.99 (Ind); 103.27 (d, ^2J(C–P) = 12.3 Hz, C_β); 109.86 (Ind); 117.82 (m, C_α); 123.91–139.27 (Ph, Ind) ppm. For **2b**: IR (KBr) ν(C≡C) 2054 and $\nu(PF_6)$ 838 cm^{-1}. ^{31}P{^{1}H} ($(CD_3)_2CO$, 121.5 MHz): δ 18.45 (d, ^5J(P–P) = 2.8 Hz, dppm); 32.05 (t, ^5J(P–P) = 2.8 Hz, PMe_3) ppm. ^{1}H ($(CD_3)_2CO$, 300 MHz): δ 1.68 (d, 9H, ^2J(H–P) = 13.0 Hz, PMe_3); 4.11 (m, 1H, PCH_2); 5.03 (m, 1H, PCH_2); 5.67 (m, 1H, Ind_5); 5.78 (m, 2H, Ind_5); 6.97–7.86 (m, 34H, Ph, Ind_6) ppm. For **2c**: IR (KBr) ν(C≡C) 2051 and $\nu(PF_6)$ 838 cm^{-1}. ^{31}P{^{1}H} ($(CD_3)_2CO$, 121.5 MHz): δ 32.14 (d, ^5J(P–P) = 3.9 Hz, PMe_3); 88.51 (d, ^5J(P–P) = 3.9 Hz, dppe) ppm. ^{1}H ($(CD_3)_2CO$, 300 MHz): δ 1.57 (d, 9H, ^2J(H–P) = 13.1 Hz, PMe_3); 2.52 (m, 4H, $P(CH_2)_2$); 5.20 (m, 1H, Ind_5); 5.64 (m, 2H, Ind_5); 7.12–7.41 (m, 34H, Ph, Ind_6) ppm. ^{13}C{^{1}H} ($(CD_3)_2CO$, 75.4 MHz): δ 7.24 (d, J(C–P) = 54.3 Hz, PMe_3); 27.15 (m, $P(CH_2)_2$); 52.48 (d, J(C–P) = 54 Hz, C_γ); 69.39, 91.95 (Ind); 99.45 (d, ^2J(C–P) = 10.7 Hz, C_β); 108.49 (Ind); 121.55 (m, C_α); 124.10–133.43 (Ph, Ind) ppm.

For **3b**: IR (KBr) ν(>C=C=C) 1865 and $\nu(PF_6)$ 840 cm^{-1}. ^{31}P{^{1}H} ($(CD_3)_2CO$, 121.5 MHz): δ 11.79 (d, ^3J(P–P) = 6.8 Hz, dppm); 26.38 (t, ^3J(P–P) = 6.8 Hz, PMe_3) ppm. ^{1}H ($(CD_3)_2CO$, 300 MHz): δ 1.54 (d, 9H, ^2J(H–P) = 12.7 Hz, PMe_3); 4.18 (m, 2H, PCH_2); 5.16 (d, 2H, J = 2.5 Hz, Ind_5); 6.10 (t, 1H, J = 2.5 Hz, Ind_5); 6.84–7.63 (m, 34H, Ph, Ind_6) ppm. ^{13}C{^{1}H} ($(CD_3)_2CO$, 75.4 MHz): δ 14.34 (d, J(C–P) = 55.2 Hz, PMe_3); 50.31 (t, J(C–P) = 21.7 Hz, PCH_2); 67.77 (Ind); 83.46 (m, C_α); 88.45 (Ind); 100.58 (d, ^2J(C–P) = 29.2 Hz, C_β); 109.34 (Ind); 124.69–138.41 (Ph, Ind); 210.81 (s, C_γ) ppm.

For **4a** (R=Ph): IR (KBr) ν(C≡C) 2074, 1953 cm^{-1}. ^{31}P{^{1}H} (C_6D_6, 121.5 MHz): δ 53.33 (s) ppm. ^{1}H (C_6D_6, 300 MHz): δ 4.64 (d, 2H, J = 2.18 Hz, Ind_5); 5.38 (t, 1H, J = 2.18 Hz, Ind_5); 6.58 (m, 2H, Ind_6); 6.86–7.75 (m, 47H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (C_6D_6, 75.4 MHz): δ 49.36 (s, CPh_2); 74.68 (Ind); 84.58, 95.20, 95.49 ($-\underline{C}\equiv\underline{C}$-Ph, Ind); 101.06 (m, C_α); 109.55 (s, C_β); 110.54, 124.45 (Ind); 126.87–148.73 (Ph, Ind) ppm.

For **5a** (R=n-C_3H_7): IR (KBr) ν(C≡C) 2078, 1943 cm^{-1}. ^{31}P{^{1}H} (C_6D_6, 121.5 MHz): δ 53.90 (s) ppm. ^{1}H (C_6D_6, 300 MHz): δ 1.03 (t, 3H, J = 7.3 Hz, CH_3); 1.60 (m, 2H, CH_2–CH_3); 2.34 (t, 2H, J = 7.1 Hz, CH_2–CH_2); 4.34 (d, 2H, J = 2.4 Hz, Ind_5); 5.10 (t, 1H, J = 2.4 Hz, Ind_5); 6.50 (m, 2H, Ind_6); 6.82 (m, 2H, Ind_6); 6.92–7.68 (m, 40H, Ph) ppm. ^{13}C{^{1}H} (C_6D_6, 75.4 MHz): δ 14.70 (CH_3); 22.37, 23.72 (CH_2–CH_2), 48.85 (CPh_2); 74.70 (Ind); 83.92, 85.82 ($-\underline{C}\equiv\underline{C}$-n-$C_3H_7$); 95.29 (Ind); 99.12 (t, ^2J(C–P) = 23.9 Hz, C_α); 110.54, 124.41 (Ind); 126.77–149.31 (Ph, Ind) ppm.

For **6a**: IR (KBr) ν(C≡C) 2058 cm^{-1}. ^{31}P{^{1}H} (C_6D_6, 121.5 MHz): δ 53.55 (s) ppm. ^{1}H (C_6D_6, 300 MHz): δ 3.50 (s, 3H, OMe); 4.59 (d, 2H, J = 2.4 Hz, Ind_5); 5.29 (t, 1H, J = 2.4 Hz, Ind_5); 6.61 (m, 2H, Ind_6); 6.83–8.00 (m, 42H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (C_6D_6, 75.4 MHz): δ 52.43 (OMe), 74.86 (Ind); 83.16 (s, C_γ); 95.68 (Ind); 105.78 (t, ^2J(C–P) = 17.6 Hz, C_α); 110.83 (Ind); 112.29 (s, C_β); 124.56 (Ind); 126.88–148.92 (Ph, Ind) ppm. For **6b**: IR (KBr) ν(C≡C) 2081 cm^{-1}. ^{31}P{^{1}H} (C_6D_6, 121.5 MHz): δ 20.05 (s) ppm. ^{1}H (C_6D_6, 300 MHz): δ 3.34 (s, 3H, OMe); 3.98 (m, 1H, PCH_2); 4.23 (m, 1H, PCH_2); 5.42 (t, 1H, J = 2.6 Hz, Ind_5); 5.48 (d, 2H, J = 2.6 Hz, Ind_5); 7.15–7.81 (m, 34H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (C_6D_6, 75.4 MHz): δ 49.54 (t, J(C–P) = 19.5 Hz, PCH_2); 51.79 (OMe); 68.64 (Ind); 82.61 (s, C_γ); 89.20, 108.37–110.30 (m, C_α; C_β, Ind); 124.16 (Ind); 126.03–148.61 (Ph, Ind) ppm. For **6c**: IR (KBr) ν(C≡C) 2086 cm^{-1}. ^{31}P{^{1}H} (C_6D_6, 121.5 MHz): δ 87.93 (s) ppm. ^{1}H (C_6D_6, 300 MHz): δ 1.75 (m, 2H, $P(CH_2)_2$); 2.15 (m, 2H, $P(CH_2)_2$); 3.05 (s, 3H, OMe); 4.89 (d, 2H, J = 2.5 Hz, Ind_5); 5.12 (t, 1H, J = 2.5 Hz, Ind_5); 6.99–7.68 (m, 34H, Ph, Ind_6) ppm. ^{13}C{^{1}H} (C_6D_6, 75.4 MHz): δ 28.34 (m, $P(CH_2)_2$); 51.70 (OMe); 70.76 (Ind); 82.62 (s, C_γ); 92.29 (Ind); 108.88–109.10 (m, C_α; C_β, Ind); 124.65, 125.40 (Ind); 126.83–148.47 (Ph) ppm.