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Preliminary Communication

Concomitant coordination of vinylidene and carbene ligands made possible at ruthenium(II) [1]

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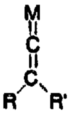
Abstract

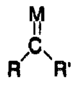
Removal of one chloride ligand from the aminocarbene *fac*-[(PNP)RuCl$_2$(C{N(H)Ph}{CH$_2$Ph})] in THF followed by treatment with phenylacetylene yields the ruthenium(II) complex *mer*-[(PNP)RuCl{C=C(H)Ph}(C{N(H)Ph}{CH$_2$Ph})]PF$_6$ (**4**). Complex **4** represents the first example of a transition metal complex with the simultaneous coordination of vinylidene and carbene ligands. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Vinylidene complexes; Carbene complexes; Aminodiphosphine ligands; Ruthenium complexes

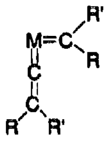
Transition-metal vinylidene complexes [1] (**I**) and heteroatom-stabilized Fischer carbene complexes [2] (**II**) are versatile reagents that exhibit a rich chemistry in both stoichiometric [1–3] and catalytic processes [3,4], particularly those involving C–C bond formation. An important reaction of this type is the benzannulation reaction of Fischer carbenes with alkynes to produce phenols [5], thiols [6] or, in the case of aminocarbenes, N-substituted benzannulated products [7]. Carbene–vinylidene species, although not detected, may also be anticipated to play a key role in the carbene–alkyne coupling [8]. However, no mononuclear transition-metal complex simultaneously containing vinylidene and carbene ligands (**III**) has been isolated. On the other hand, complexes with two unsaturated M=C moieties are extremely rare, being limited to the octahedral bis-alkenylallenylidene ruthenium derivative [(dppm)$_2$Ru{C=C=C(OMe)CH=CPh$_2$}$_2$](BF$_4$)$_2$ [9], where two allenylidene ligands are *trans* to each other.



I



II



III

We have recently reported the synthesis of the Ru(II)-vinylidene complexes *fac*- and *mer*-[(PNP)RuCl$_2${C=C(H)R}] [PNP = CH$_3$CH$_2$CH$_2$N(CH$_2$CH$_2$PPh$_2$)$_2$; R = Ph, *p*-tolyl] [10]. The M=C=C moiety in these complexes is susceptible to attack by water and amines (ammonia, primary and secondary amines) to give C–C bond cleavage via hydrolysis and aminolysis reactions, respectively [11,12]. The aminolysis reactions can be stopped at the stage of amine addition to give aminocarbenes of the formula *fac*-[(PNP)RuCl$_2$(C{N(H)R}{CH$_2$Ph})] (R = alkyl, aryl) [12].

Herein, we report that the aminocarbene complexes are excellent precursors to the isolation of unprecedented mixed vinylidene–aminocarbene complexes. This reaction is here exemplified for the synthesis of *mer*-[(PNP)RuCl{C=C(H)Ph}(C{N(H)Ph}{CH$_2$Ph})]PF$_6$ (**4**) (Scheme 1).

Addition of aniline to a dichloromethane solution of the vinylidene complex **1** at room temperature under a protective dinitrogen atmosphere gives yellow crystals of the aminocarbene *fac*-[(PNP)RuCl$_2$(C{N(H)Ph}{CH$_2$Ph})] [2] (**2**)

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[1] Dedicated to Professor Ivano Bertini in recognition of his important contribution to coordination chemistry and his commitment to maintaining the excellence of the Florentine School of Inorganic Chemistry.

[2] Synthesis and characterization of **2**: a three-fold excess of freshly distilled aniline was added at room temperature to a stirred solution of complex **1** (0.40 g, 0.53 mmol) in 30 ml of dichloromethane. The reaction mixture was stirred in the dark overnight during which time all the starting vinylidene complex dissolved to give a canary yellow solution which was evaporated to ~5 ml. Addition of light petroleum ether (b.p. 40–60°C) gave canary yellow microcrystals of **2** which were recrystallized from CH$_2$Cl$_2$ and light petroleum ether. Yield 92%. *Anal.* Calc. for C$_{45}$H$_{48}$N$_2$Cl$_2$P$_2$Ru: C, 63.53; H, 5.69; N, 3.29. Found: C, 63.44; H, 5.56; N, 3.21%. IR: ν(NH) 3466 (br.

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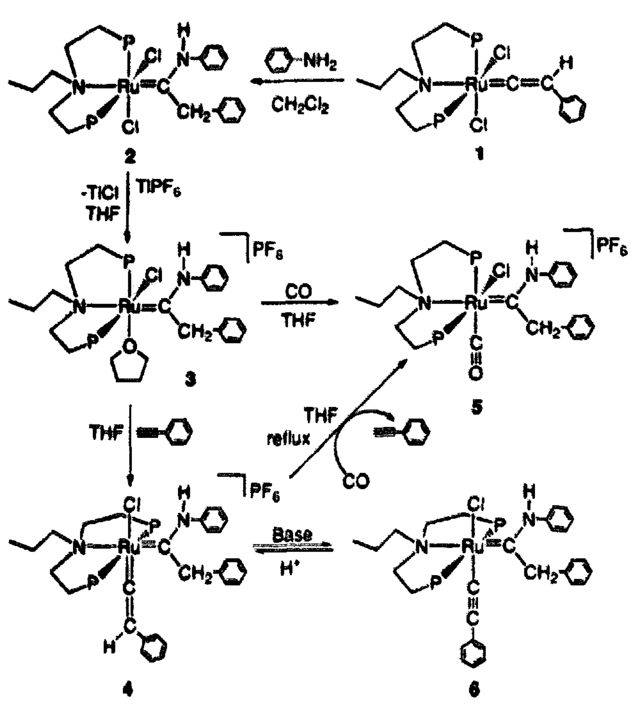

Scheme 1.

in very good yield. Reaction of **2** with one equiv. of $TlPF_6$ in anhydrous THF affords a yellowish solution of the THF adduct *fac*-[(PNP)RuCl(THF)(C{N(H)Ph}{CH_2Ph})]PF_6 [3] (**3**). This complex reacts smoothly with phenylacetylene at room temperature to give off-white crystals of **4** [4]. The ^1H NMR spectrum contains the typical resonances of both aminocarbene (δ_{NH} 11.78, br s) and vinylidene (δ_{CH} 3.80, t, $^4J_{HP}$ 2.4 Hz) protons. In keeping with this structural assignment, the $^{13}C\{^1H\}$ NMR spectrum contains two well-resolved triplets at δ 356.2 (C_α vinylidene, $^2J_{CP}$ 13.7 Hz) and 253.4 (carbene C atom, $^2J_{CP}$ 8.9 Hz). The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at 35.70 ppm as expected for a meridional arrangement of the aminodiphosphine ligand [10]. Finally, the IR spectrum of **4** shows the characteristic $\nu(C{=}C)$ absorption of the vinylidene ligand at 1624 cm^{-1}. Formation of **4** most likely occurs following the displacement of the weakly coordinated THF ligand by phenylacetylene through 1-alkyne to vinylidene tautomerization, a reaction which is well documented for d^6 ruthenium complexes [1,10].

Complex **4** is endowed with a rich reactivity which is currently under scrutiny. Preliminary reactivity tests (Scheme 1) indicate that the vinylidene ligand is more labile and more acidic than the aminocarbene ligand. Indeed, vinylidene to acetylene retrotautomerization takes place when **4** is refluxed with CO in THF to give the carbonyl complex [(PNP)RuCl(CO)(C{N(H)Ph}{CH_2Ph})]PF_6 (**5**) [5], while mild bases bring about the reversible, selective deprotonation of **4** to give the alkynyl–aminocarbene complex [(PNP)RuCl{C≡CPh}(C{N(H)Ph}{CH_2Ph})] (**6**) [6].

The isolation of **4** (and similar derivatives) [7] shows that mixed vinylidene–aminocarbene complexes can exist as stable species and could be relevant to modelling mechanistic steps in several important processes such as benzannulation reactions [3b], Fischer–Tropsch synthesis [13], and alkene metathesis [14].

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w) cm^{-1}. $^{31}P\{^1H\}$ NMR (22°C, $CDCl_3$, 121.42 MHz): 51.31 (s); ^1H NMR (22°C, CD_2Cl_2, 299.94 MHz): δ_{NH} 12.35 (s, 1H), δ_{CH_2Ph} 4.88 (s, 2H). $^{13}C\{^1H\}$ NMR (20°C, $CDCl_3$, 75.42 MHz): $\delta_{Ru=C}$ 264.9 (t, $^2J_{CP}$ 11.7 Hz), δ_{CH_2Ph} 59.8 (s).

[3] Synthesis and characterization of **3**: one equiv. of $TlPF_6$ (350 mg, 1.00 mmol) was added with vigorous stirring to a THF (15 ml) solution of **2** (850 mg, 1.00 mmol) under nitrogen. After 30 min, $^{31}P\{^1H\}$ NMR analysis of the solution revealed the complete transformation of **2** into **3**. This solution can be used, after filtering through a cotton plug to remove TlCl, for further preparative purposes. Isolation of **3** as a beige powder can be obtained by addition of n-hexane and slow evaporation under nitrogen. Yield 78%. *Anal.* Calc. for $C_{49}H_{56}N_2ClF_6OP_3Ru$: C, 56.96; H, 5.47; N, 2.71. Found: C, 56.52; H, 5.31; N, 2.49%. IR: ν(NH) 3279 (br, w); ν(PF) 834 (br, s) cm^{-1}. $^{31}P\{^1H\}$ NMR (22°C, CD_2Cl_2, 81.01 MHz): 65.04 (s); ^1H NMR (22°C, CD_2Cl_2, 200.13 MHz): δ_{NH} 10.05 (s, 1H), δ_{CH_2Ph} 4.74 (s, 2H).

[4] Synthesis and characterization of **4**: a solution of **3**, prepared as described in footnote 3, was treated with an excess of phenylacetylene (1.00 ml, 9.10 mmol). The solution was stirred for 3 h and then n-hexane (20 ml) was added. Slow evaporation of the solvent gave off-white microcrystals of **4**. Yield 85%. *Anal.* Calc. for $C_{53}H_{54}N_2F_6ClP_3Ru$: C, 59.87; H, 5.12; N, 2.64. Found: C, 59.79; H, 5.04; N, 2.77%. IR: ν(NH) not observed; ν(PF) 846 (br, s) cm^{-1}. $^{31}P\{^1H\}$ NMR (22°C, $CDCl_3$, 81.01 MHz): 35.70 (s); ^1H NMR (22°C, $CDCl_3$, 200.13 MHz): δ_{NH} 11.78 (s, 1H), δ_{CH_2Ph} 4.67 (s, 2H), $\delta_{C=CH}$ 3.80 (t, $^4J_{HP}$ 2.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (22°C, $CDCl_3$, 50.32 MHz): $\delta_{Ru-C(vinylidene)}$ 356.2 (t, $^2J_{CP}$ 13.7 Hz), $\delta_{Ru-C(carbene)}$ 253.4 (t, $^2J_{CP}$ 8.9 Hz), $\delta_{Ru=C=C}$ 108.7 (t, $^3J_{CP}$ 2.3 Hz), δ_{CH_2Ph} 61.6 (s).

[5] Synthesis and characterization of **5**: 0.200 mg of **4** (0.19 mmol) were dissolved in THF (10 ml) under a CO atmosphere. The solution was slowly brought to reflux and heating was maintained for 30 min. Cooling to room temperature and addition of n-hexane (20 ml) gave pale yellow microcrystals of **5**. Yield 80%. Alternatively, **5** can be prepared in almost quantitative yield from **2** after removal of one chloride ligand with $TlPF_6$ under a CO stream. *Anal.* Calc. for $C_{46}H_{48}N_2ClF_6OP_3Ru$: C, 55.86; H, 4.90; N, 2.83. Found: C, 55.73; H, 4.91; N, 2.64%. IR: ν(NH) 3294 (br, vw), ν(CO) 2000 (vs), ν(PF) 842 (br, s) cm^{-1}. $^{31}P\{^1H\}$ NMR (22°C, $CDCl_3$, 81.01 MHz): AB system δ_A 46.51, δ_B 27.70 ($^2J_{PP}$ 26.5 Hz); ^1H NMR (22°C, $CDCl_3$, 200.13 MHz): δ_{NH} 11.02 (s, 1H), δ_{CH_2Ph} AB system, δ_A 6.18, δ_B 6.09, J_{HAHB} 15.2 Hz). $^{13}C\{^1H\}$ NMR (22°C, $CDCl_3$, 50.32 MHz): $\delta_{Ru-C(carbene)}$ 255.1 (t, $^2J_{CP}$ 9.1 Hz), δ_{CO} 199.3 (dd, $^2J_{CP(trans)}$ 97.3, $^2J_{CP(cis)}$ 14.1 Hz), δ_{CH_2Ph} 67.4 (s).

[6] Synthesis and characterization of **6**: neat tert-butylamine (100 μl, 0.95 mmol) was syringed into a stirred solution of **4** (0.200 mg, 0.19 mmol) in THF (10 ml). After ~20 min the solution was diluted with n-hexane (20 ml) and concentrated under nitrogen to give **6** (yellow powder). Yield 80%. *Anal.* Calc. for $C_{53}H_{53}N_2ClP_2Ru$: C, 69.41; H, 5.83; N, 3.06. Found: C, 69.22; H, 5.87; N, 2.85%. IR: ν(NH) 3410 (br, vw), ν(C≡C) 2081 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (22°C, acetone-d_6, 81.01 MHz): δ 43.22 (s); ^1H NMR (22°C, acetone-d_6, 200.13 MHz): δ_{NH} 11.29 (s, 1H), δ_{CH_2Ph} 4.90 (br s, 2H).

[7] Preliminary tests confirm that the formation of vinylidene–aminocarbenes similar to **4** is a general reaction for the aminocarbene complexes [(PNP)$RuCl_2$(C{N(H)R}{CH_2Ph})] [12] with 1-alkynes.

References

[1] For a review see M.I. Bruce, Chem. Rev., 91 (1991) 197.

[2] H. Fischer, F.R. Kreissl, U. Schubert, P. Hoffman, K.H. Dötz and K. Weiss, In Transition Metal Carbenes, VCH, Weinheim, 1983.

[3] (a) M.P. Doyle, in E.W. Abel, F.G. Stone and G. Wilkinson (eds.), Comprehensive Organometallic Chemistry II, Pergamon, Oxford, Vol. 12, 1995, Chs. 5.1–5.2; (b) W.D. Wulff, in E.W. Abel, F.G. Stone and G. Wilkinson (eds.), Comprehensive Organometallic Chemistry II, Pergamon, Oxford, Vol. 12, 1995, Ch. 5.3; (c) L.S. Hegedus, in E.W. Abel, F.G. Stone and G. Wilkinson (eds.), Comprehensive Organometallic Chemistry II, Pergamon, Oxford, Vol. 12, 1995, Ch. 5.4; (d) J.R. Stille, in E.W. Abel, F.G. Stone and G. Wilkinson (eds.), Comprehensive Organometallic Chemistry II, Pergamon, Oxford, Vol. 12, 1995, Ch. 5.5.

[4] Leading articles reporting on catalytic processes involving vinylidene complexes: (a) S.J. Landon, P.M. Shulman and G.L. Geoffroy, J. Am. Chem. Soc., 107 (1985) 6739; (b) T.J. Katz, T.-H. Ho, N.-Y. Shih, Y.-C. Ying and V.I. Stuart, J. Am. Chem. Soc., 106 (1984) 2659; (c) Y. Sasaki and P.H. Dixneuf, J. Chem. Soc., Chem. Commun., (1986) 790; (d) R. Mahé, Y. Sasaki, C. Bruneau and P.H. Dixneuf, J. Org. Chem., 54 (1989) 1518; (e) B.M. Trost, G. Dykera and R.J. Kulawiec, J. Am. Chem. Soc., 112 (1990) 7809; (f) C. Bianchini, M. Peruzzini, C. Frediani, F. Zanobini and A. Albinati, J. Am. Chem. Soc., 113 (1991) 5453; (g) C. Bianchini, M. Peruzzini, P. Frediani, A. Polo and F. Zanobini, Inorg. Chim. Acta, 220 (1994) 5; (h) B.M. Trost, Chem. Ber., 129 (1996) 1313; and Refs. therein.

[5] K.H. Dötz, Angew. Chem., Int. Ed. Engl., 23 (1984) 587.

[6] W.D. Wulff, in L.S. Liebeskind (ed.), Advances in Metal–Organic Chemistry, Vol. 1, JAI Press, Greenwich, CT, 1989, p. 238.

[7] See for example: B.A. Anderson, W.D. Wulff, T.S. Powers, S. Tribbit and A.L. Rheingold, J. Am. Chem. Soc., 114 (1992) 10784.

[8] For lead references on the mechanism of the benzannulation reaction see: (a) M. Brookhart, M.B. Humphrey, H.J. Kratzer and G.O. Nelson, J. Am. Chem. Soc., 102 (1980) 7803; (b) H. Fischer, J. Mühleimer, R. Märkl and K.H. Dötz, Chem. Ber., 115 (1982) 1355; (c) H.C. Foley, L.M. Strubinger, T.S. Targos and G.L. Geoffroy, J. Am. Chem. Soc., 105 (1983) 3064; (d) P. Hoffmannn and M. Hämmerle, Angew. Chem., Int. Ed. Engl., 28 (1989) 908; (e) K.E. Garrett, J.B. Sheridan, D.B. Pourreau, W.C. Feng, G.L. Geoffry, D.L. Staley and A.L. Rheingold, J. Am. Chem. Soc., 111 (1989) 8383; (f) K.H. Dötz, T. Schäfer, F. Kroll and K. Harms, Angew. Chem., Int. Ed. Engl., 31 (1992) 1236; (g) B.A. Anderson, W.D. Wulff and A.L. Rheingold, J. Am. Chem. Soc., 112 (1990) 8615; (h) H. Fischer, J. Hofmann and E. Mauz, Angew. Chem., Int. Ed. Engl., 30 (1991) 998; (i) B.A. Anderson, J. Bao, T.A. Brandvold, C.A. Challener, W.D. Wulff, Y.-C. Xu and A.L. Rheingold, J. Am. Chem. Soc., 115 (1993) 10671; (j) M.F. Gross and M.G. Finn, J. Am. Chem. Soc., 116 (1994) 10921.

[9] (a) N. Pirio, D. Touchard, P.H. Dixneuf, M. Fettouhi and L. Ouahab, Angew. Chem., Int. Ed. Engl., 31 (1992) 651; (b) D. Touchard, N. Pirio, L. Toupet, M. Fettouhi, L. Ouahab and P.H. Dixneuf, Organometallics, 14 (1995) 5263.

[10] C. Bianchini, P. Innocenti, M. Peruzzini, A. Romerosa and F. Zanobini, Organometallics, 15 (1996) 272.

[11] C. Bianchini, J.A. Casares, M. Peruzzini, A. Romerosa and F. Zanobini, J. Am. Chem. Soc., 118 (1996) 4585.

[12] C. Bianchini, M. Peruzzini, A. Romerosa and F. Zanobini, Organometallics, 14 (1995) 3152.

[13] (a) G.A. Olah and A. Molnár, Hydrocarbon Chemistry, Wiley, New York, 1995, Ch. 3, pp. 66–73; (b) M.L. Turner, H.C. Long, A. Shenton, P.K. Byers and P.M. Maitlis, Chem. Eur. J., 1 (1995) 549; and Refs. therein; (c) E.L. Hoel, G.B. Anselt and S. Leta, Organometallics, 5 (1986) 585; (d) E.L. Hoel, Organometallics, 5 (1986) 587.

[14] See for example: J.C. Mol, in B. Cornils and W.A. Herrmann (eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, VCH, Weinheim, 1996, Ch. 2.3.3, pp. 318–332.