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Communications

Cationic Vinyl and Dicationic Carbene Ruthenium(II) Complexes from a Vinylidene(hydrido) Precursor

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Summary: The reaction of the vinylidene(hydrido)ruthenium(II) compound $[RuHCl({=}C{=}CH_2)(PCy_3)_2]$ (**1a**) *with excess* KPF_6 *in* CH_2Cl_2/CH_3CN *affords the five-coordinate vinyl complex* $[Ru(CH{=}CH_2)(CH_3CN)_2(PCy_3)_2]PF_6$ (**2a**), *which on treatment with* $NaBPh_4$ *or* $NaB(Ar_f)_4$ *gives the tetraaryloborate salts* **2b** *and* **2c** *in excellent yields. The six-coordinate compounds* $[Ru(CH{=}CHPh)(CH_3CN)_3(PiPr_3)_2]X$ (**3a**, $X = Cl$; **3b**, $X = PF_6$) *were obtained in a similar route using* $[RuHCl({=}C{=}CHPh)(PiPr_3)_2]$ (**1b**) *as the starting material. Protonation of* **2c** *or* **2d** ($X = BF_4$) *with, respectively,* $[H(OEt_2)_2]B(Ar_f)_4$ *or* HBF_4 *yields* $[Ru({=}CHCH_3)(CH_3CN)_2(PCy_3)_2]X_2$ (**4a**,**b**), *which to the best of our knowledge represent the first dicationic carbeneruthenium(II) complexes.*

Recently, we reported[1] that the reaction of the hydrido(vinylidene) compound $[RuHCl({=}C{=}CH_2)(PCy_3)_2]$ (**1a**) with acids HA, containing an anion that does *not* coordinate to the metal center, in diethyl ether affords instead of the anticipated cationic carbene derivative $[RuCl({=}CHCH_3)(PCy_3)_2]^+$ the corresponding carbyne(hydrido) complex $[RuHCl({\equiv}CCH_3)(PCy_3)_2(OEt_2)]^+$. This cation catalyzes with high efficiency not only the ring-opening metathesis polymerization of cyclooctene but also the cross-olefin metathesis of cyclopentene with methylacrylate.[1] Since the lifetime of the carbyne(hydrido)ruthenium cation is limited and significantly lower than that of the corresponding neutral carbene $[RuCl_2({=}CHCH_3)(PCy_3)_2]$,[2] we attempted to prepare more stable carbyneruthenium(II) species by using stronger σ-donors than diethyl ether. In the context of these studies we observed that the starting material **1a** can be easily converted, in the presence of acetonitrile, to cationic vinylruthenium(II) compounds which react with acids HA to give dicationic five-coordinate ruthenium carbenes.

Treatment of a solution of **1a** in CH_2Cl_2/CH_3CN with excess KPF_6 leads to a gradual change of color from brown-yellow to brown and results in the formation of the vinyl complex **2a** in 87% isolated yield.[3] Salt metathesis of **2a** with $NaBPh_4$ in methanol affords **2b** (Scheme 1), the molecular structure of which has been determined by X-ray crystallography.[4]

As shown in Figure 1, the coordination geometry around the metal center of the cation corresponds to that of a square pyramid with the two phosphines and the two acetonitriles *trans* disposed. The atoms C5 and C6 of the vinyl ligand (which occupies the apical position) lie in the same plane as the nitrogen and carbon atoms of the CH_3CN units. In contrast to the almost linear N1−Ru−N2 axis, the P1−Ru−P2 axis is slightly bent with the phosphorus atoms pointing away

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[1] Stüer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem.* **1998**, *110*, 3603−3606; *Angew. Chem., Int. Ed.* **1998**, *37*, 3421−3423.

[2] (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem.* **1995**, *107*, 2179−2181; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

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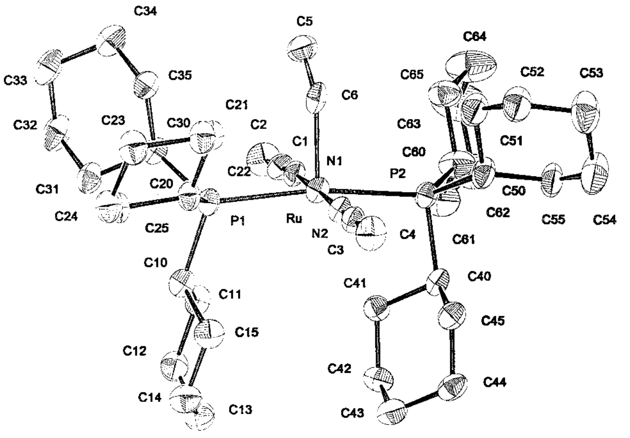
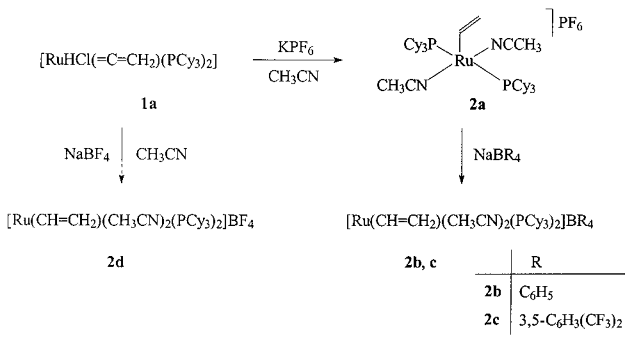
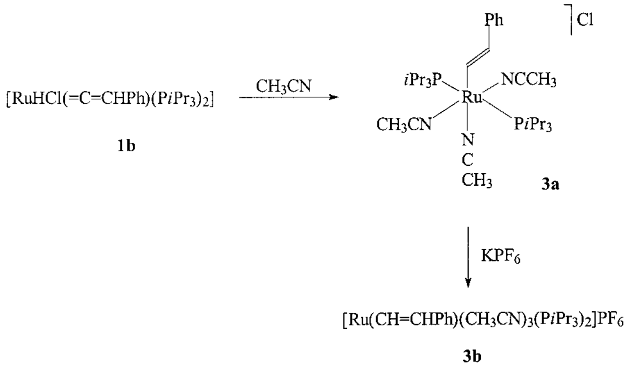


Figure 1. Molecular structure (ORTEP plot) of compound **2b**, with anisotropic uncertainty parameters depicting 50% probability. Selected bond distances (Å) and angles (deg): Ru−C6 2.001(5), Ru−N1 2.008(4), Ru−N2 2.006(4), Ru−P1 2.3975(13), Ru−P2 2.3979(12), C5−C6 1.340(7), N1−C1 1.160(6), N2−C3 1.142(6); C6−Ru−P1 92.48(12), C6−Ru−P2 96.24(12), C6−Ru−N1 92.35(16), C6−Ru−N2 89.52(16), N1−Ru−N2 178.05(15), P1−Ru−P2 171.04(4), N1−C1−C2 178.7(5), N2−C3−C4 179.0(5).

Scheme 1



Scheme 2



from the $CH{=}CH_2$ moiety. The distance Ru−C6 of 2.001 (5) Å is relatively short but comparable to that found in other ruthenium compounds with a Ru−C(sp^2) bond.[5]

The bis(triisopropylphosphine) complex **1b** behaves similarly to **1a** and reacts with acetonitrile in CH_2Cl_2 to give **3a** (Scheme 2). Treatment of **3a** with KPF_6 affords the more stable PF_6 salt **3b**, which was isolated as an orange solid in 75% yield.[6] Both the elemental analyses and the spectroscopic data of **3a**,**b** confirm that in contrast to **2a**,**b** *three* acetonitrile ligands are coordinated to the metal center. The smaller cone angle of P*i*Pr_3 (160°) compared to PCy_3 (170°)[7] probably favors the increase of the coordination number from five to six in the Ru(P*i*Pr_3)$_2$ derivative. An uncharged six-coordinate ruthenium compound of composition $[RuCl_2(CH_3CN)_2(P\mathit{i}Pr_3)_2]$ has recently been prepared by Ozawa et al. from $[(p\text{-cymene})RuCl_2]_2$ and P*i*Pr_3 in toluene/acetonitrile.[8] Moreover, Caulton et al. found that the hydrido(iodo) complex $[RuHI({=}C{=}CHSiMe_3)(P\mathit{t}Bu_2Me)_2]$ reacts with excess methylisocyanide to give the substituted vinylruthenium(II) derivative $[Ru(CH{=}CHSiMe_3)(CNMe)_3(P\mathit{t}Bu_2Me)_2]I$.[9]

While the protonation of **2a** or **2b** with excess HBF_4/OEt_2 gives a saltlike product with $[Ru({=}CHCH_3)(CH_3CN)_2(PCy_3)_2]^{2+}$ as the cation and different ratios of, respectively, PF_6^-/BF_4^- and BPh_4^-/BF_4^- as the anion, the reaction of **2c**[3] with Brookhart's acid[10] $[H(OEt_2)_2]B(Ar_f)_4$ (Ar_f = 3,5-bis(trifluoromethyl)phenyl) affords cleanly the bis(tetraaryloborate) **4a** in 91% yield (Scheme

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(3) The preparation of **2a** is as follows. A solution of **1a** (270 mg, 0.30 mmol) in 30 mL of CH_2Cl_2/CH_3CN (1:1) was treated with KPF_6 (250 mg, 1.36 mmol) and stirred for 35 min at room temperature. The solvent was removed, and the residue was extracted twice with 10 mL of CH_2Cl_2 each. The combined extracts were evaporated in vacuo, and the remaining red-brown solid was washed twice with pentane (8 mL) and dried: yield 307 mg (87%); mp 55 °C dec; Λ (CH_3NO_2) 68.6 $cm^2\ \Omega^{-1}\ mol^{-1}$; IR (KBr) ν(CN) 2253 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.38 (dd, J(HH) = 7.9 and 15.8 Hz, 1H, C$H{=}CH_2$), 4.84 (d, J(HH) = 7.9 Hz, 1H, one H of CH_2, *cis* to C*H*), 4.70 (d, J(HH) = 15.8 Hz, 1H, one H of CH_2, *trans* to CH), 2.49 (s, 6H, CH_3CN), 2.24−1.22 (m, 66H, C_6H_{11}); ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 150.2 (br s, RuCH), 125.5 (s, CN), 117.3 (s, $={}CH_2$), 34.3 (vt, N = 16.2 Hz, CH of C_6H_{11}), 29.7, 26.5 (both s, C_6H_{11}), 28.1 (vt, N = 10.2 Hz, $CHCH_2$ of C_6H_{11}), 5.0 (s, CH_3CN); ^{31}P NMR (162.0 MHz, CD_2Cl_2) δ 22.4 (s, PCy_3), −144.0 (sept, J(PF) = 709.4 Hz, PF_6^-). Compound **2b** was prepared from **2a** (450 mg, 0.40 mmol) and $NaBPh_4$ (200 mg, 0.58 mmol) in 20 mL of methanol: orange solid; yield 416 mg (78%); mp 100 °C dec; Λ (CH_3NO_2) 62.5 $cm^2\ \Omega^{-1}\ mol^{-1}$. Compound **2c** was prepared from **2a** (54 mg, 0.06 mmol) and $NaB(Ar_f)_4$ (55 mg, 0.06 mmol) in 10 mL of ether at 0 °C: red-brown solid; yield 94 mg (97%); mp 70 °C dec; Λ (CH_3NO_2) 78.2 $cm^2\ \Omega^{-1}\ mol^{-1}$. Compound **2d** was prepared analogously as described for **2a**, from **1a** (101 mg, 0.14 mmol) and $NaBF_4$ (250 mg, 2.28 mmol) in 15 mL of CH_2Cl_2/CH_3CN (2:1): orange-red solid; yield 109 mg (91%); mp 52 °C dec; Λ (CH_3NO_2) 57.8 $cm^2\ \Omega^{-1}\ mol^{-1}$.

(4) Crystal data for **2b**: crystals from CH_2Cl_2; triclinic, $P\bar{1}$ (No. 2), $a = 12.7193(17)$ Å, $b = 15.482(2)$ Å, $c = 17.447(2)$ Å, $\alpha = 88.771(16)°$, $\beta = 79.931(15)°$, $\gamma = 69.452(15)°$, $V = 3164.3(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.227$ g cm^{-3}, $T = 173(2)$ K, μ(Mo Kα) = 0.423 cm^{-1}; data collected on a Stoe IPDS diffractometer using Φ scan mode ($2\theta_{max} = 50.06°$); 25 291 reflections scanned, 10 533 unique, 6204 observed ($I > 2\sigma(I)$); extinction parameter 0.0051(5), 686 parameters refined to give $R = 4.95\%$ and $R_w = 12.80\%$ with a reflex-parameter ratio of 15.4 and a residual electron density +1.064/−0.948 e Å^{-3}.

(5) Daniel, T.; Mahr, N.; Braun, T.; Werner, H. *Organometallics* **1993**, *12*, 1475−1477.

(6) The preparation of **3a** and **3b** is as follows. A solution of **1b** (81 mg, 0.14 mmol) in 8 mL of CH_2Cl_2 was treated with acetonitrile (3 mL) and stirred for 5 min at room temperature. The solvent was evaporated in vacuo, and the residue was washed repeatedly with pentane (5 mL) and dried. A light yellow solid of **3a** was obtained: yield 87 mg (93%); mp 59 °C dec; Λ (CH_3NO_2) 55.8 $cm^2\ \Omega^{-1}\ mol^{-1}$. A sample of **3a** (85 mg, 0.12 mmol) was dissolved in 8 mL of CH_2Cl_2/CH_3CN (5:3) and then treated with KPF_6 (150 mg, 0.81 mmol). After stirring for 30 min at room temperature, the reaction mixture was worked up as described for **2a**: orange solid; yield 73 mg (75%); mp 36 °C dec; IR (KBr) ν(CN) 2260 cm^{-1}; ^1H NMR (200 MHz, CD_2Cl_2) δ 8.56 (d, J(HH) = 16.8 Hz, 1H, C$H{=}CHPh$), 7.14, 6.92 (both m, 5H, C_6H_5), 6.34 (d, J(HH) = 16.8 Hz, 1H, $CH{=}CHPh$), 2.46 (m, 6H, PCHCH_3), 2.42 (s, 6H, CH_3CN), 2.31 (s, 3H, CH_3CN), 1.27 (m, 36H, PCHCH_3); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 159.7 (br s, RuCH), 141.2 (s, *ipso*-C of C_6H_5), 133.3 (s, $={}CHPh$), 128.2, 123.6, 123.1 (all s, C_6H_5), 125.4 (s, CN), 24.1 (vt, N = 17.1 Hz, P$CHCH_3$), 19.1 (s, PCHCH_3), 5.0, 3.3 (both s, CH_3CN); ^{31}P NMR (81.0 MHz, CD_2Cl_2) δ 28.3 (s, P*i*Pr_3), −144.0 (sept, J(PF) = 709.4 Hz, PF_6^-).

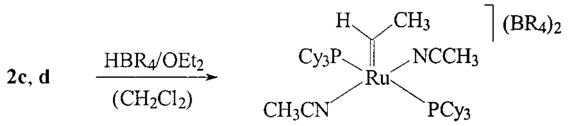
(7) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(8) Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190−5196.

(9) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091−3100.

(10) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920−3922.

Scheme 3



4a, b	R
4a	3,5-$C_6H_3(CF_3)_2$
4b	F

3).[11] Analogously, the bis(tetrafluoroborate) **4b** was prepared on treatment of **2d** with an excess of a solution of HBF_4 in ether. Both **4a** and **4b** are yellow, moderately air-stable solids, the conductivity of which (in nitromethane) corresponds to that of 1:2 electrolytes. Regarding the spectroscopic data, the most typical features are the signal for the $=CH$ carbene proton at δ 17.20 (**4a**) or 17.70 (**4b**) in the ^1H NMR and the multiplet for the carbene carbon atom at δ 335.1 (**4a**) in the ^{13}C NMR spectrum. The single resonance for the phosphorus nuclei at δ 41.0 (**4a**) or 38.0 (**4b**) in the ^{31}P NMR spectra indicates that the phosphine ligands are stereochemically equivalent and therefore in *trans* disposition. Attempts to generate the dication $[Ru(=CHCH_3)(CH_3CN)_2(PCy_3)_2]^{2+}$ from $[RuCl_2(=CHCH_3)(PCy_3)_2]$ by substitution of the chloride ligands for acetonitrile failed. It should be mentioned that, to the best of our knowledge, compounds **4a** and **4b** are the first *dicationic* five-coordinate carbeneruthenium complexes described as yet.

The formation of a metal carbene from a metal vinyl precursor is not without precedence. Casey and Helquist showed already in 1982 that neutral cyclopentadienyliron compounds with $CR=CH_2$ as ligand can be converted with HBF_4 to corresponding cationic carbene derivatives.[12] Similar transformations of neutral vinyl to monocationic carbene complexes via attack of an electrophile at the β-carbon atom of the vinyl ligand have since been carried out by Gladysz and others.[13] We note, however, that as far as we know, there is no report about the preparation of a *dicationic* carbene complex from a *monocationic* vinylmetal precursor by protonation. Our present interests are aimed to find out whether **4a** or **4b** can be used, in the absence or in the presence of a Lewis acid, as catalysts for olefin metathesis.

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Supporting Information Available: A table with the elemental analysis of compounds **2a**–**2d**, **3a**, **3b**, and **4a** as well as fully labeled diagrams and tables of crystallographic data, data collection and solution and refinement details, positional and thermal parameters, and both distances and angles for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] The preparation of **4a** was as follows. A solution of **2c** (94 mg, 0.06 mmol) in 8 mL of CH_2Cl_2 was treated with a solution of $[H(OEt_2)_2]B(Ar_f)_4$ (58 mg, 0.06 mmol) in 4 mL of CH_2Cl_2 at 0 °C. After the solution was stirred for 5 min, it was warmed to room temperature and the solvent was removed in vacuo. The yellow residue was washed three times with 5 mL portions of pentane and dried: yield 130 mg (91%); mp 130 °C dec; Λ (CH_3NO_2) 138.9 $cm^2\ \Omega^{-1}\ mol^{-1}$; ^1H NMR (400 MHz, CD_2Cl_2) δ 17.20 (q, J(HH) = 5.9 Hz, 1H, $=CHCH_3$), 7.72 (s, 16H, *ortho*-H of Ar_f), 7.57 (s, 8H, *p*-H of Ar_f), 2.87 (d, J(HH) = 5.9 Hz, 3H, $=CHCH_3$), 2.75 (s, 6H, CH_3CN), 2.17–1.23 (m, 66H, C_6H_{11}); ^{13}C NMR (100.6 MHz, acetone-d_6) δ 335.1 (m, Ru=C), 163.0 (d, J(BC) = 49.6 Hz, *ipso*-C of Ar_f), 135.9 (s, *ortho*-C of Ar_f), 130.4, 118.8 (both m, *meta*- and *para*-C of Ar_f), 125.7 (q, J(FC) = 272.1 Hz, CF_3), 48.5 (s, $=CHCH_3$), 35.3 (vt, N = 19.1 Hz, CH of C_6H_{11}), 30.8, 26.1 (both s, C_6H_{11}), 28.5 (vt, N = 10.2 Hz, $CHCH_2$ of C_6H_{11}), 5.7 (s, CH_3CN); ^{31}P NMR (162.0 MHz, acetone-d_6) δ 41.0 (s). Compound **4b** was prepared from **2d** (275 mg, 0.32 mmol) in CH_2Cl_2 (8 mL) and an excess of HBF_4 (ca. 1.60 mmol) in ether: yellow solid; yield 225 mg (75%); mp 55 °C dec; Λ (CH_3NO_2) 98.8 $cm^2\ \Omega^{-1}\ mol^{-1}$; IR (KBr) ν(CN) 2275 cm^{-1}.

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