ChemComm

The first organoruthenium(IV) complexes containing nitrogen donor ligands by oxidative addition of allylic substrates to coordinatively unsaturated Ru(II) complexes†

Hideo Kondo, Yoshitaka Yamaguchi and Hideo Nagashima*

Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816-8580, Japan and CREST, Japan Science and Technology Corporation (JST), Japan. E-mail: nagasima@cm.kyushu-u.ac.jp

Received (in Cambridge, UK) 12th April 2000, Accepted 8th May 2000

Oxidative addition of allylic substrates to coordinatively unsaturated ruthenium(II), (η^5-C_5Me_5)Ru(amidinate) complexes, afford cationic ruthenium(IV) compounds, [(η^5-C_5Me_5)Ru(amidinate)(η^3-allyl)]$^+$, which have been characterized by spectroscopic analysis and X-ray structure determination.

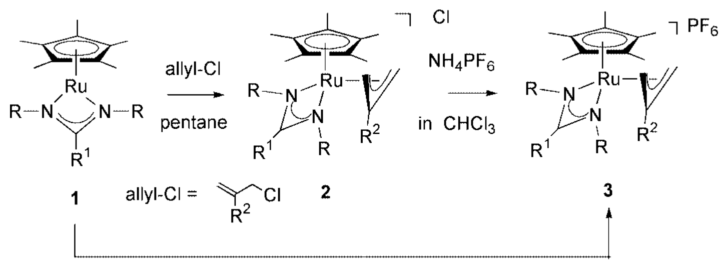
Studies on the structures and reactions of coordinatively unsaturated transition metal complexes have received much attention from organometallic chemists, because these compounds are believed to be involved in many transition metal-mediated organic reactions as important intermediates.[1] In particular, the structures and reactions of coordinatively unsaturated ruthenium(II) complexes have been actively investigated recently;[1] these studies contribute to the understanding of the factors leading to the stabilization of these complexes, *e.g.* steric effects, presence of π-donor ligands, metal-bond strength and their tendency towards oxidative addition of H_2 and $HSiR_3$.[1–3] Although the oxidative addition of allylic substrates to ruthenium(II) complexes[4] is an important elementary reaction in the catalytic transformation of an allyl moiety,[5] that to isolated coordinatively unsaturated ruthenium compounds has not, as yet, been studied.[1–3] We have recently reported a novel reactive complex, (η^5-C_5Me_5)Ru(amidinate) **1**, which shows signs of coordinative unsaturation, in which the amidinate ligand contributes to stabilizing the formally 16-electron configuration.[6] The fact that **1** is highly reactive towards the reaction with a variety of two-electron donor ligands stimulated us to explore the possibility that **1** may also be reactive towards oxidative addition reactions.[6] Here, we report that **1** readily reacts with an allylic substrate to give the corresponding cationic Ru(IV) allylic compound as shown in Scheme 1. This is the first example, to the best of our knowledge, of oxidative addition of allylic substrates to isolable coordinatively unsaturated ruthenium complexes. Additionally, the product is a rare example of an organoruthenium(IV) compound coordinated to nitrogen donor ligands.

Complex **1a** was treated with a stoichiometric amount of allyl chloride at −78 °C and the mixture was allowed to warm to room temperature. After 1 h, the solvent was removed *in vacuo*. Spectroscopic evidence suggests that the resulting yellow solid is [(η^5-C_5Me_5)Ru(amidinate)(η^3-allyl)]Cl **2a** (yield of the crude product >95%) containing *ca.* 5% of (η^5-C_5Me_5)Ru(η^3-allyl)Cl_2.[4a] This new η^3-allyl complex **2a** is not very stable in solution and gradually decomposes to a mixture of intractable products. In contrast, **3a**, a stable analogue of **2a**, was successfully isolated as a yellow solid in 48% yield by exchange in $CHCl_3$ of the counter anion Cl^- to PF_6^- followed by recrystallization of the crude product. Complex **3a** could also be obtained directly from **1a** by treatment with allyl chloride in the presence of $NaPF_6$. The oxidative addition of allyl acetate or allyl methyl carbonate in the presence of $NaPF_6$ offers an alternative synthetic method for **3a** without formation of by-products; **3a** was isolated in quantitative yield. In a similar fashion, **3b**, a methallyl analogue of **3a**, and a compound **3c**, bearing a different amidinate ligand, were successfully prepared and characterized as shown in Table 1.

Table 1

Precursor	R^2	X	Method	Product	Isolated yield (%)
1a	H	Cl	A	**3a**	48
1a	Me	Cl	A	**3b**	55
1c	H	Cl	A	**3c**	62
1a	H	Cl	B	**3a**	64
1a	Me	Cl	B	**3b**	39
1c	H	Cl	B	**3c**	62
1a	H	OCOMe	B	**3a**	97
1a	H	OCO_2Me	B	**3a**	97

Complex **3a** was fully characterized by spectroscopic methods (^1H NMR, ^{13}C NMR, IR),‡ elemental analyisis and an X-ray crystal structure determination§ and an ORTEP drawing of **3a** is shown in Fig. 1. Complex **3a** has a square-pyramidal structure, with two nitrogen atoms of the amidinate ligand and terminal carbons of the η^3-allyl ligand at the basal positions. The orientation of the allyl group is *endo*, and variable temperature NMR studies showed that there is no equilibrium with the corresponding *exo* isomer. This *endo* orientation is also seen in (η^5-C_5Me_5)Ru(η^3-allyl)X_2 reported previously.[4a] The crystal structure of **3a**, in comparison with that of the starting



Scheme 1 Method A; allyl–Cl in pentane followed by NH_4PF_6 in $CHCl_3$; method B; allyl–X (X = Cl, OAc, OCO_2Me) and $NaPF_6$ in THF. For **1**–**3**: **a**, R = Bu^t, R^1 = Ph, R^2 = H; **b**, R = Bu^t, R^1 = Ph, R^2 = Me; **c**, R = Pr^i, R^1 = Me, R^2 = H.

---

† Electronic supplementary information (ESI) available: typical procedures and spectroscopic data. See http://www.rsc.org/suppdata/cc/b0/b002927k/

DOI: 10.1039/b002927k

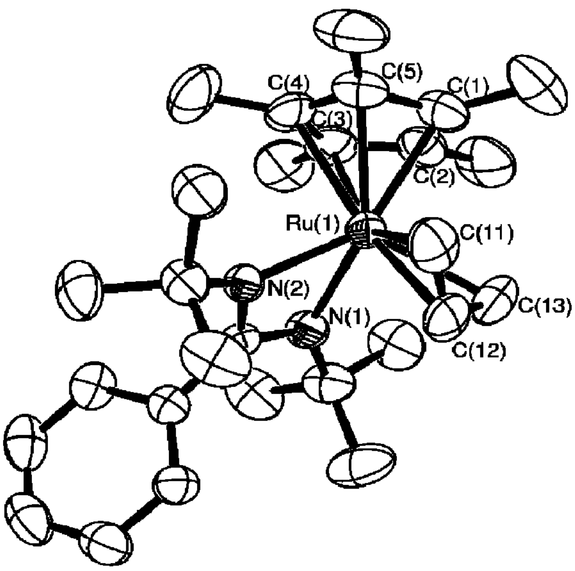
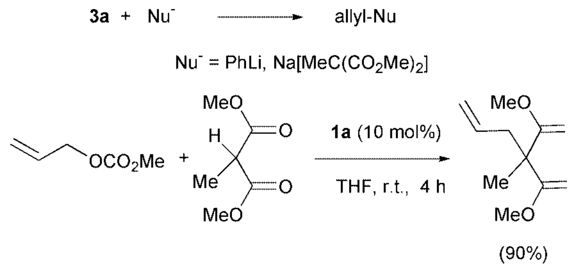


Fig. 1 ORTEP drawing of **3a** showing 50% thermal ellipsoids. PF_6^- omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–C(1–5)$_{av}$ 2.263(4), Ru(1)–N(1), 2.128(3), Ru(1)–N(2) 2.125(3), Ru(1)–C(11) 2.193(5), Ru(1)–C(12) 2.132, Ru(1)–C(13) 2.206, C(11)–C(12) 1.385(8), C(12)–C(13) 1.379(8); N(1)–Ru(1)–N(2) 61.98(12), C(11)–Ru(1)–C(12) 64.1(2), C(11)–C(12)–C(13) 115.2(5).

material **1a** reveals that the Ru–N and Ru–C bonds (average) become longer [**1a**: Ru–N 2.073(3) Å, Ru–C$_{av}$ 2.158(4) Å].

The chemical reactivity of the η^3-allyl moiety is an interesting problem for the exploration of stoichiometric and catalytic reactions mediated by **1** or **2**. Preliminary studies on the reactivity of **3a** revealed that it reacted with nucleophiles such as PhLi and sodium dimethyl methylmalonate but not with electrophiles such as aldehydes and unsaturated molecules such as ethylene and CO. The stoichiometric reaction of **3a** with PhLi in THF gave a mixture of 1-phenylprop-1-ene and 1-phenylprop-2-ene in a ratio of 1:2. Similarly, treatment of **3a** with sodium dimethyl methylmalonate resulted in formation of dimethyl allylmethylmalonate. In both of the reactions, regeneration of **1a** was also observed. The latter allylation reaction can be extended to a catalytic reactions when allyl methyl carbonate is used as the allylic substrate; **1a** (10 mol%) successfully catalyzed the reaction of allyl methyl carbonate with dimethyl methyl malonate in THF at room temperature to give the product in 90% yield (Scheme 2).

In conclusion, oxidative addition of allylic substrates to the isolable coordinatively unsaturated complex (η^5-C_5Me_5)Ru(η-amidinate), has been observed which leads to a new cationic organoruthenium(IV) complex [(η^5-C_5Me_5)Ru(η^3-allyl)(η-amidinate)]$^+$ stabilized by a nitrogen-donor ligand. This oxidative addition is envisioned to be extendable to stoichiometric and catalytic transformations of allylic substrates mediated by **1**–**3**, as already evidenced by our preliminary studies on the reactions of **3a** with nucleophiles.



Scheme 2

We are grateful to Kouki Matsubara (Kyushu Univ.) for his help in the X-ray analyses. Part of this work is financially supported by the Japan Society of the Promotion of Science (Grant-in-Aid for Scientific Research 10450343).

Notes and references

‡ Representative spectroscopic evidence: **3a**; ^{1}H NMR ($CDCl_3$): δ 0.95 [s, 18H, $C(CH_3)_3$], 1.81 [s, 15H, $C_5(CH_3)_5$], 2.22 (d, J = 10.2 Hz, 2H, *anti*-CH of the allyl group), 4.53 (d, J = 6.1 Hz, 2H, *syn*-CH of the allyl group), 5.36 (dt, J = 6.1, 10.2 Hz, 1H, central-CH of the allyl group), 7.16 (m, 1H, C_6H_5), 7.24 (m, 1H, C_6H_5), 7.32 (m, 1H, C_6H_5), 7.35 (m, 1H, C_6H_5), 7.44 (m, 1H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.9 [$C_5(CH_3)_5$], 35.5 [$C(CH_3)_3$], 58.0 [$C(CH_3)_3$], 59.7 (CH_2 of the allyl group), 97.2 (CH of the allyl group), 106.6 [$C_5(CH_3)_5$], 127.4, 127.6, 127.8, 129.9, 132.8, 138.6 (C_6H_5), 178.9 (NCN). Anal. Calc. for $C_{28}H_{43}N_2PF_6Ru$: C, 51.45; H, 6.63; N, 4.29. Found: C, 51.22; H, 6.62; N, 4.34%.

§ *Crystal data* for $C_{28}H_{43}F_6N_2PRu$ **3a**: M = 653.68, orthorhombic, space group *Pbca*, a = 31.771(6), b = 14.038(4), c = 13.366(5) Å, V = 5961(3) Å^3, T = 293 K, Z = 8, μ = 0.637 mm^{-1}, 6849 reflections measured, 6848 unique (R_{int} = 0.0409), 4403 observed ($>2\sigma$), final residuals $R1$ = 0.0492, $wR2$ = 0.1418 [$I > 2\sigma(I)$]; $R1$ = 0.0917, $wR2$ = 0.1620 (all data). CCDC 182/1633. See http://www.rsc.org/suppdata/cc/b0/b002927k/ for crystallographic files in .cif format.

1 For a recent extensive review, see: R. Poli, *Chem. Rev.*, 1996, **96**, 2135 and references therein.

2 For a review on coordinatively unsaturated Ru(II) complexes, see: K. G. Caulton, *New. J. Chem.*, 1994, **18**, 25 and references therein.

3 For recent studies of coordinatively unsaturated ruthenium(II) complexes stabilized by nitrogen donor ligands, see the following literature and references cited therein: C. Gemel, K. Mereite, R. Schmid and K. Kirchner, *Organometallics*, 1997, **16**, 5601; K.-J. Haack, S. Hayashi, A. Fujii, T. Ikariya and R. Noyori, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 285; C. Gemel, J. C. Huffman, K. G. Caulton, K. Mauthner and K. Kirchner, *J. Organomet. Chem.*, 2000, **593**, 342.

4 (*a*) H. Nagashima, K. Mukai and K. Itoh, *Organometallics*, 1984, **3**, 1314; H. Nagashima, K. Mukai, Y. Shiota, K. Yamaguchi, K. Ara, T. Fukahori, H. Suzuki, M. Akita, Y. Moro-oka and K. Itoh, *Organometallics*, 1990, **9**, 799; (*b*) M. O. Albers, D. C. Liles, D. J. Robinson, A. Shaver and E. Singleton, *Organometallics*, 1987, **6**, 2347; (*c*) P. J. Fagan, W. S. Mahoney, J. C. Calabrese and I .D. Williams, *Organometallics*, 1990, **9**, 1843; (*d*) E. Rüba, W. Simanko, K. Mauthner, K. M. Soldouzi, C. Slugovc, K. Mereiter, R. Schmid and K. Kirchner, *Organometallics*, 1999, **18**, 3843 and references therein.

5 T. Kondo, H. Ono, N. Sataka, T. Mitsudo and Y. Watanabe, *Organometallics*, 1995, **14**, 1945; T. Kondo, Y. Morisaki, S. Uenoyama, K. Wada and T. Mitsudo, *J. Am. Chem. Soc.*, 1999, **121**, 8657 and references therein.

6 Y. Yamaguchi and H. Nagashima, *Organometallics*, 2000, **19**, 725.