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Communications

A Stable Three-Coordinate Rhodium(I) Olefin Complex

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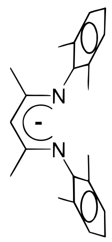
Summary: Reaction of **L**Li *(*$\mathbf{L} = \mathrm{ArNC(Me)CHC(Me)NAr}$*, Ar* $= 2,6\text{-}\mathrm{Me_2C_6H_3}$*) with* $[\mathrm{Rh(COE)_2Cl}]_2$ *(COE = cyclooctene) produces stable, three-coordinate* **L***Rh(COE) (***1***). At room temperature in solution, the* **L***Rh fragment moves rapidly over one face of the COE ligand via reversible allyl hydride formation.*

Generation of a vacant coordination site is a key step in many catalytic reactions. Therefore, organometallic species with a vacant site are of profound interest. However, such species are highly reactive and cannot usually be isolated and characterized; instead, their involvement must be inferred indirectly, e.g., by trapping experiments or kinetic studies.

In this communication, we report the isolation, characterization, and reactivity of a stable, three-coordinate rhodium(I) olefin complex. The ancillary ligand that makes this possible is the β-diiminate ligand **L**.[1] β-Diimine ligands are becoming more popular since the discovery of "Brookhart-type" Ni and Pd polymerization catalysts.[2]



The aryl groups of **L**, which are forced by their substitution pattern to be nearly perpendicular to the ligand backbone, severely limit the space around the metal atom. For ligands that fit within this space, like 1,5-cyclooctadiene, this results in efficient shielding of the system: light yellow **L**Rh(COD)[3] is exceedingly stable and does not react with, for example, hydrogen peroxide (room temperature) or hydrogen (100 °C). Two ethylene ligands also fit within the available space, but olefin rotation in $\mathbf{L}\mathrm{Rh(C_2H_4)_2}$ is completely blocked.[4] However, two *cis*-disubstituted olefins do not fit. The substituents cannot point *out*ward because of the steric ligand constraints. They cannot point *in*ward either, because then they would hinder each other. Indeed, reaction of **L**Li with $[\mathrm{Rh(COE)_2Cl}]_2$ (COE = cyclooctene)

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[1] A few rhodium derivatives of less hindered diiminates have been reported: Jarvis, A. C.; Raymond, R. D. W.; Kemmitt, D. W. *J. Organomet. Chem.* **1977**, *136*, 121. Howden, M. E.; Kemmitt, R. D. W.; Schilling, M. D. *J. Chem. Soc., Dalton Trans.* **1980**, 1716. Brunner, H.; Rahman, A. F. M. M. *Z. Naturforsch.* **1983**, *38b*, 1332. See also: Brown, J. M.; Guiry, P. J.; Price, D. W.; Hursthouse, M. B.; Karalulov, S. *Tetrahedron: Asymmetry* **1994**, *5*, 561.

[2] See e.g.: Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514. Rahim, M.; Taylor, N. J.; Xin, S.; Collins, S. *Organometallics* **1998**, *17*, 1315.

[3] **L**Rh(COD), prepared from **L**Li(THF) and $[\mathrm{Rh(COD)Cl}]_2$. NMR ($\mathrm{CDCl_3}$) ^{1}H (200 MHz) 1.55 (**1**), 5.10 (**3**), 6.97−7.11 (m, *m*+*p*), 2.31 (*o*-$C\mathrm{H_3}$), 3.01 (br, C*H*═CH), 2.12, 1.60 (CH_2); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (50.3 MHz) 25.5 (**1**), 159.3 (**2**), 97.8 (**3**), 150.9 (*i*), 132.9 (*o*), 128.7 (*m*), 124.9 (*p*), 19.3 (*o*-$C\mathrm{H_3}$), 79.8 (*C*H═CH, $J_{\mathrm{RhC}} = 13$ Hz), 31.1 ($C\mathrm{H_2}$). Further details of the synthesis and characterization of this and further compounds are given in the Supporting Information.

[4] $\mathbf{L}\mathrm{Rh(C_2H_4)_2}$, prepared from **L**Li(THF) and $[\mathrm{Rh(C_2H_4)_2Cl}]_2$. NMR ($\mathrm{C_6D_6}$) ^{1}H (200 MHz) 1.65 (**1**), 5.30 (**3**), 7.04−7.12 (m, *m*+*p*), 2.41 (*o*-$C\mathrm{H_3}$), 2.62 and 2.01 (m, $\mathrm{C_2}H_4$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (50.3 MHz) 25.9 (**1**), 159.5 (**2**), 98.9 (**3**), 150.4 (*i*), 133.0 (*o*), 129.2 (*m*), 125.7 (*p*), 19.8 (*o*-$C\mathrm{H_3}$), 63.3 ($C_2\mathrm{H_4}$, $J_{\mathrm{RhC}} = 11$ Hz).

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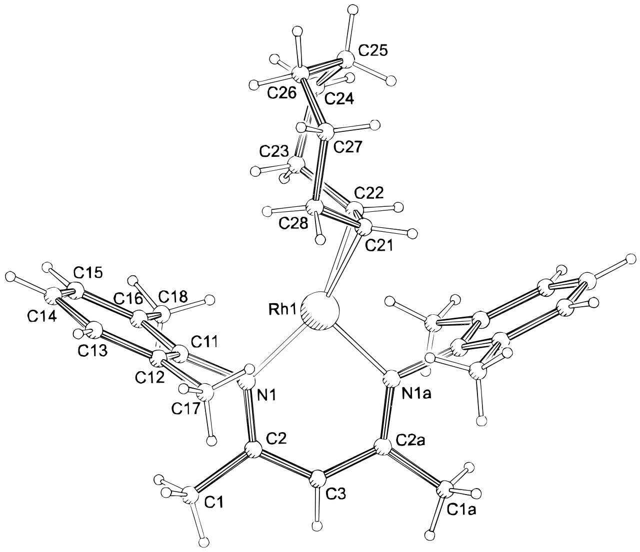

Figure 1. X-ray structure of **1**. The complex is located over a 2-fold axis through Rh1 and C3, with disorder in carbon atoms C21, C22, C23, and C28; only one image of these is shown. Atom labels ending in "a" indicate images related by the 2-fold axis. Selected bond lengths (Å) and angles (deg): Rh1−N1 1.955(2), Rh1−C21 2.072(5), Rh1−C22 2.066(6), C21−C22 1.398(7), N1−Rh1−N1a 91.3(1), N1a−Rh1−C21 111.0(2), N1a−Rh1−C22 110.8(2).

produces the stable, deep purple mono-olefin complex **L**Rh(COE) (**1**).[5]

The X-ray structure of **1** (Figure 1)[6] shows a three-coordinate T-shaped structure. The hydrogen positions could not be determined, but inspection of the COE carbon skeleton shows that none of them could be very close to the fourth coordination site.[7] In solution (C_6D_{12} or THF-d_8) at room temperature, only two broadened resonances (ratio 6:8) are observed for the COE fragment, and the diiminate ligand has apparent C_{2v} symmetry. On cooling to −80 °C, several separate COE resonances can be observed; also, the left and right halves of the ligand (Figure 1) become inequivalent, as expected for the static structure. We believe that the dynamic process responsible for this behavior is an equilibration of olefin and allyl hydride structures.[8] We have investigated the olefin and allyl hydride isomers of the model system ($C_3N_2H_5$)Rh(propene) theoretically.[9] The structure calculated for the allyl hydride has C_s symmetry, with the hydride located in the open face of the allyl group (Figure 2). Thus, the hydride can move back to either terminal carbon of the allyl group. For the COE complex, this results in movement of the **L**Rh fragment over one face of the COE ligand. Because this process does not exchange *endo* and *exo* COE hydrogens (the olefinic hydrogens count as *exo*), these are observed as separate resonances in the room-temperature NMR spectra. According to the calculations, the olefin structure is slightly lower in energy than the allyl hydride, and the barrier between them is small (see Table 1), in qualitative agreement with the NMR data.

Table 1. Calculated Relative Energies (kcal/mol) for the Isomerization of ($C_3N_2H_5$)M(C_3H_6) (M = Rh, Ir)

M	(propene)	TS	(allyl)(H)
Rh	(0)	+12.2	+8.1
Ir	+3.5	(n.d.)	(0)

Interestingly, the corresponding iridium compound **2**[10] is *not* fluxional at room temperature. Moreover, the ^{1}H spectrum clearly shows that it prefers the allyl hydride structure ($\delta_{\mathrm{IrH}} = -46$ ppm).[11] Our calculations also indicate a slight preference of the Ir complex for an allyl hydride structure (Table 1). Unfortunately, this compound is not very stable, and we could not study its possible fluxionality at higher temperatures. Crabtree[12] and Carmona[13] prepared a series of trispyrazolylborate iridium(III) allyl hydride complexes via allylic activation of olefins. Like 16-e complex **2**, their 18-e allyl hydride complexes were found to be nonfluxional at room temperature. The different behavior of the Ir and Rh complexes is in agreement with general trends of third-row vs second-row elements: preference for higher oxidation states and higher barriers to rearrangements.

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[5] Complex **1**: ^{1}H NMR (200 MHz, C_6D_{12}, RT) 1.72 (**1**), 5.18 (**3**), 7.0−7.1 (m, *m*+*p*), 2.65 (*o*-CH_3), 1.87 (br s, 8H), 0.34 (br s, 6H) c-octene; (500 MHz, THF-d_8, −80 °C) 1.55, 1.39 (**1**,**1′**), 4.95 (**3**), 7.16, 7.10 (*m*,*m′*), 7.06, 7.05 (*p*,*p′*), 2.70, 2.39 (*o*,*o′*-CH_3), 2.48 (C*H*=CH), 2.08, 1.5, 1.2, 1.0 (br, CH_2); ^{13}C{^{1}H} NMR (125.7 MHz, THF-d_8, −80 °C) 24.1 (**1**), ≈26.5 (**1′**, overlap with solvent), 158.6, 156.3, 154.3, 150.9 (**2**,**2′**,*i*,*i′*), 100.4 (**3**, J_{RhC} = 39 Hz), 134.6, 134.5 (*o*,*o′*), 129.9, 129.5 (*m*,*m′*), 126.2, 125.8 (*p*,*p′*), 21.1, 20.4 (*o*,*o′*-CH_3), 64.8 (br,*C*H=CH), 31.6 (br,*C*H_2), remaining CH_2 groups not observed.

[6] Crystal data for **1** ($C_{29}H_{39}N_2Rh$): fw = 518.53, monoclinic *C*2/*c*, a = 13.3646(7) Å, b = 15.2454(6) Å, c = 12.8589(6) Å, β = 93.521(4)°, Z = 4, V = 2615.0(2) Å^3, d_{calcd} = 1.317 g cm^{-3}, $R(F)$ = 0.0353, $R_w(F^2)$ = 0.0882 ($I_o > 2\sigma(I_o)$). For further details, see the Supporting Information.

[7] If hydrogens are placed at calculated positions, the two closest allylic hydrogens are at distances of 2.79 and 2.96 Å from the rhodium atom, and the two closest xylyl hydrogens are at 3.06 and 3.13 Å.

[8] The allyl hydride mechanism is one of the accepted mechanisms for olefin isomerization. However, only a few examples of rapid equilibration between the two structures have been reported: Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871. Bönneman, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 736. Decomposition of rhodium(III) allyl hydride complexes to free olefin has also been demonstrated: Nixon, J. F.; Wilkins, B. *J. Organomet. Chem.* **1972**, *44*, C25; **1974**, *80*, 129.

[9] All calculations were carried out with the program ADF (Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. Versluis, L.; Ziegler, T. H. *Chem. Phys.* **1988**, *88*, 322. te Velde, G.; Baerends, E. J. *J. Comput. Chem.* **1992**, *99*, 84. Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87) using frozen cores; calculations on the Ir system were quasi-relativistic (Boerrigter, P. M. Ph.D. Thesis, Free University, Amsterdam, 1987. Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050). The basis set employed was DZ+P on H, C, and N and a valence basis of 3 s, 3 p, and 1 p functions on the metal atoms. The VWN exchange−correlation potential (Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200) was used in combination with Becke−Perdew nonlocal corrections (Becke, A. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406, 8822). A spin-restricted formalism was used throughout. Geometries were optimized without any symmetry restrictions. Reductive elimination from palladium(II) and platinum(II) allyl hydrides has been studied computationally: Sakaki, S.; Satoh, H.; Shono, H.; Ujino, Y. *Organometallics* **1996**, *15*, 1713.

[10] Complex **2**: NMR (THF-d_8, −20 °C) ^{1}H (400 MHz) 1.70 (**1**), 5.37 (**3**), 7.20, 7.18 (d, *m*+*m′*), 6.99 (t, *p*), 2.16, 2.21 (*o*,*o′*-CH_3), 5.40 (t, 1H), 2.54 (br q, 2H) (c-octenyl C*H*), 1.90, 1.27, 1.05, 0.82, 0.25 (br m, CH_2), −46.19 (Ir*H*); ^{13}C{^{1}H} (100.6 MHz) 23.9 (**1**), 157.6 (**2**), 103.2 (**3**), 157.2 (*i*), 132.7, 130.9 (*o*,*o′*), 130.2, 129.8 (*m*,*m′*), 126.0 (*p*), 20.3, 20.0 (*o*,*o′*-*C*H_3), 84.9, 49.6 (c-octenyl *C*H), 32.8, 30.3, 19.9 (*C*H_2).

[11] Several batches of crystals of **2** have been prepared, but all showed severe twinning problems. The low-quality data obtained from the best crystal confirmed the expected connectivity of the complex and showed an arrangement of the cyclooctenyl group relative to the diimine fragment similar to the calculated structure shown in Figure 2C, but the data were too poor to allow derivation of meaningful geometrical parameters.

[12] Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444.

[13] Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860.

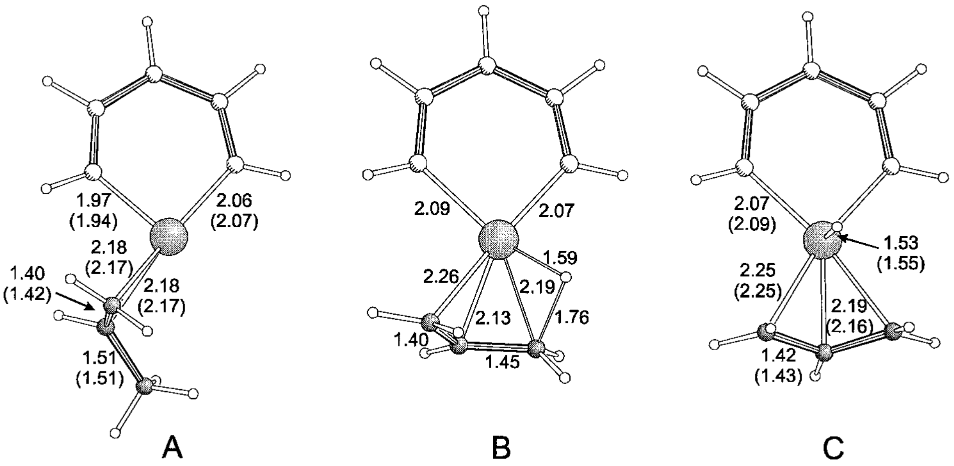

Figure 2. Calculated structures of olefin complex (A), transition state (B), and allyl hydride form (C) for the model system $(C_3N_2H_5)Rh(C_3H_6)$; bond lengths in angstroms for the Rh(Ir) system.

The coordinative unsaturation of complex **1** is illustrated by its (reversible) reaction with nitrogen. Under 1 bar of nitrogen, the brown dinitrogen complex **L**Rh(COE)(N_2) is formed rapidly and quantitatively ($\nu_{NN} = 2172$ cm^{-1}). This is no longer fluxional, and the NMR spectra show the expected resonances for a static COE complex.[14] However, on evacuation of the solution the deep purple color of the three-coordinate species is restored and the N−N stretch vibration disappears. Addition of 1-hexene to **1** also results in formation of a brownish complex. We formulate this as four-coordinate **L**Rh(COE)(hexene), since like the dinitrogen complex it reverts to **1** on evacuation.

The above results demonstrate that complex **1** offers a unique opportunity to study the "chemistry of an empty site". The further reactivity of this unusual unsaturated species will be reported in due course.

Supporting Information Available: Details of syntheses of complexes **L**Rh(COD), **L**Rh(C_2H_4)$_2$, **L**Rh(COE) (**1**), **L**Rh(COE)(N_2), and **L**Ir(cyclo-octenyl)(H) (**2**), analytical data for these complexes, and details of the X-ray structure determination of **1** (11 pages). Ordering information is given on any current masthead page.

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(14) **L**Rh(COE)(N_2): NMR (THF-d_8) ^{1}H (500 MHz) 1.56, 1.75 (**1**,**1′**), 5.24 (**3**), 7.16, 7.15 (d, *m*,*m′*), 7.04, 7.09 (t, *p*,*p′*), 2.50, 2.32 (*o*,*o′*-C*H*$_3$), 3.04 (C*H*=CH), 2.14, 1.59, 1.2 (br, C*H*$_2$); ^{13}C{^{1}H} (125.7 MHz) 26.6, 23.8 (**1**,**1′**), 160.3, 159.1 (**2**,**2′**), 99.9 (**3**, $J_{RhC} = 11$ Hz), 156.2, 150.0 (*i*,*i′*), 134.8, 133.3 (*o*,*o′*), 130.1, 29.8 (*m*,*m′*), 127.1, 126.6 (*p*,*p′*), 20.6, 20.1 (*o*,*o′*-*C*H$_3$), 76.7 (*C*H=CH, $J_{RhC} = 11$ Hz), 32.5, 30.8, 28.1 (*C*H$_2$).