Keywords: allyl complexes · calcium · main group elements · structure elucidation

[1] T. P. Hanusa, *Polyhedron* **1990**, *9*, 1345 – 1362.
[2] T. P. Hanusa, *Chem. Rev.* **1993**, *93*, 1023 – 1036.
[3] F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless, B. Royo, *J. Chem. Soc. Chem. Commun.* **1991**, 724 – 726.
[4] C. Eaborn, S. A. Hawkes, P. B. Hitchcock, J. D. Smith, *Chem. Commun.* **1997**, 1961 – 1962.
[5] J. S. Overby, T. P. Hanusa, *Organometallics* **1996**, *15*, 2205 – 2212.
[6] J. S. Overby, T. P. Hanusa, *Angew. Chem.* **1994**, *106*, 2300 – 2302; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2191 – 2193.
[7] G. Mösges, F. Hampel, P. v. R. Schleyer, *Organometallics* **1992**, *11*, 1769 – 1770.
[8] A. Yanagisawa, S. Habaue, H. Yamamoto, *J. Am. Chem. Soc.* **1991**, *113*, 8955 – 8956.
[9] A. Yanagisawa, S. Habaue, K. Yasue, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 6130 – 6141.
[10] G. Fraenkel, A. Chow, W. R. Winchester, *J. Am. Chem. Soc.* **1990**, *112*, 1382 – 1386.
[11] Crystal structure data of $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$: tetragonal, space group $P4_2/n$, $a = 14.7796(1)$, $c = 16.5390(1)$ Å, $V = 3612.72(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.021$ g cm^{-3}, $M_r = 555.17$. Refinement of 3212 reflections collected at the University of Minnesota at 173 ± 2 K with $I > 2.0\sigma(I)$ led to residuals of $R(F^2) = 0.0605$ and $R_w(F^2) = 0.1204$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102493. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[12] M. Marsch, K. Harms, W. Massa, G. Boche, *Angew. Chem.* **1987**, *99*, 706 – 707; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 696 – 697.
[13] N. van E. Hommes, M. Bühl, P. von R. Schleyer, Y.-D. Wu, *J. Organomet. Chem.* **1991**, *409*, 307 – 320.
[14] R. A. Williams, T. P. Hanusa, J. C. Huffman, *Organometallics* **1990**, *9*, 1128 – 1134.
[15] D. J. Burkey, E. K. Alexander, T. P. Hanusa, *Organometallics* **1994**, *13*, 2773 – 2786.
[16] A. E. Smith, *Inorg. Chem.* **1972**, *11*, 165 – 170.
[17] N. W. Murrall, A. J. Welch, *J. Organomet. Chem.* **1986**, *301*, 109 – 130.
[18] Full geometry optimization (HF/6-31G*) was performed assuming C_s symmetry; the SCF implementation provided in the MacSpartan *Plus* package (Wavefunction, Inc., Irvine, CA, USA) was used. Other geometric features of note: C–C 1.391 Å, C_{allyl}–Si 1.811 Å, C-C-Si 125.8°.
[19] R. Goddard, C. Krüger, F. Mark, R. Stansfield, X. Zhang, *Organometallics* **1985**, *4*, 285 – 290.

Amidation of $[Rh^I(ethene)]^+$ via a 2-Rhodaoxetane

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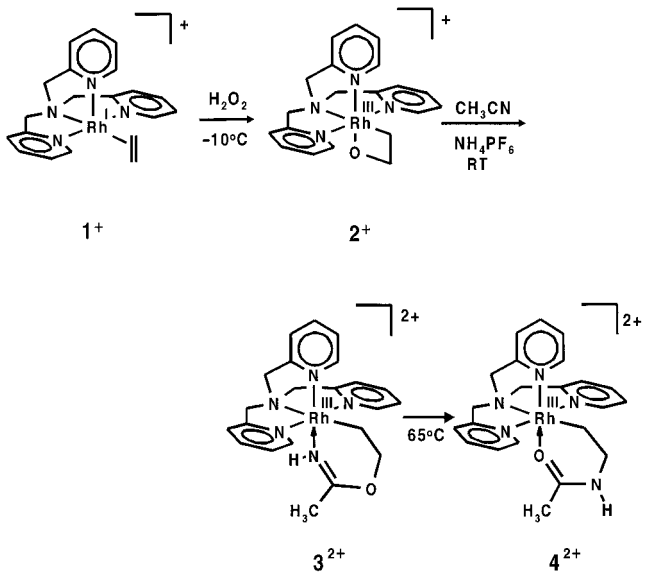
The formation of a C–N bond from an olefin and an amine or amide is a very desirable transformation.[1] A catalytic version of this reaction could be a valuable alternative to classical industrial preparations of amines or amides. However, the few catalytic examples reported so far for this reaction are either slow or limited in scope (specific substrate or intramolecular reaction).[2] Therefore, any new approach to formation of C–N bonds from olefins is of great interest. In this context we wish to report the two-step formation of a C–N bond from an olefin, with hydrogen peroxide and a nitrile (as an amide equivalent), via a 2-rhodaoxetane (1-oxa-2-rhodacyclobutane) complex.

Recently, we described the oxidation of $[(tpa)Rh^I(ethene)]^+$, $\mathbf{1}^+$, (tpa = *N*,*N*,*N*-tri(2-pyridylmethyl)amine) with H_2O_2 to the 2-rhodaoxetane $\mathbf{2}^+$ (Scheme 1).[3] The isolation of $\mathbf{2}^+$ gave us the unique opportunity to study the reactivity of an



Scheme 1. Step-wise amidation of the Rh^I(ethene) complex $\mathbf{1}^+$; oxidation with H_2O_2 to 2-rhodaoxetane $\mathbf{2}^+$, formation of imino ester $\mathbf{3}^{2+}$ by reaction with NH_4^+/MeCN, and thermal rearrangement to amide $\mathbf{4}^{2+}$.

unsubstituted 2-metallaoxetane.[4, 5] The 2-rhodaoxetane $\mathbf{2}^+$ is stable in neat CH_3CN. However, addition of one mole of NH_4PF_6 per mole of $\mathbf{2}^+$ to a solution of $\mathbf{2} \cdot BPh_4$ in CH_3CN at room temperature results in quantitative conversion into the dicationic imino ester $\mathbf{3}^{2+}$ within four hours (Scheme 1). We

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precipitated pure $\mathbf{3}\cdot(BPh_4)_2\cdot 1.5\,H_2O$ by addition of $NaBPh_4$ and MeOH. Crystals of $\mathbf{3}\cdot(BPh_4)_2\cdot MeOH$ that were suitable for X-ray diffraction were obtained by crystallization from a saturated solution of DMSO layered with MeOH. The crystal structure of $\mathbf{3}^{2+}$[6] shows that the O,C-coordinated 2-oxyethyl fragment in $\mathbf{2}^{+}$ has been converted into a N,C-coordinated 2-(acetimidoyloxy)ethyl fragment, which is in accordance with the NMR data (see Table 1). The acetimidoyl-NH fragment of $\mathbf{3}^{2+}$ shows a clear NOE contact with the nearby axial NCH_2-Py protons in the ^{1}H NOESY spectrum.

Table 1. Selected NMR data for $\mathbf{2}^{+}$, $\mathbf{3}^{2+}$, and $\mathbf{4}^{2+}$.[a]

	$\mathbf{2}^{+}$ Y = O	$\mathbf{3}^{2+}$ Y = O	$\mathbf{4}^{2+}$ Y = N
^{1}H NMR:			
(δ)Rh*C*H_2CH$_2$Y	2.37	3.38	3.47
(^2J(Rh,H))	(2.4)	(2.7)	(2.4)
RhCH$_2$*C*H_2Y	4.92	4.26	3.23
(^3J(H,H))	(7.5)	(5.6)	(5.9)
^{13}C NMR:			
(δ)Rh*C*H$_2$CH$_2$Y	1.3	28.5	33.3
(^1J(Rh,C))	(18.4)	26.6)	(27.7)
RhCH$_2$*C*H$_2$Y	78.7	71.8	41.5
(^2J(Rh,C))	(4.0)	(0)	(0)

[a] ^{1}H NMR: in CD_3CN; ^{13}C NMR: in [D$_6$]acetone ($\mathbf{2}^{+}$) or in [D$_6$]DMSO ($\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$).

The ^{1}H NMR spectrum recorded immediately after the addition of NH_4PF_6 to a solution of $\mathbf{2}\cdot BPh_4$ in CD_3CN shows (besides signals of $\mathbf{2}^{+}$ and $\mathbf{3}^{2+}$) signals indicative of the presence of a C-coordinated 2-hydroxyethyl group.[7] It seems, therefore, that the reaction proceeds via the intermediate 2-hydroxyethyl complex $[(tpa)Rh^{III}(CH_2CH_2OH)(MeCN)]^{2+}$ $\mathbf{2a}^{2+}$, which results from protonation of the 2-rhodaoxetane oxygen atom and solvation by MeCN. This complex rearranges to imino ester $\mathbf{3}^{2+}$ by addition of the 2-hydroxyethyl group to the activated C≡N bond of the coordinated CH_3CN molecule.[8] This rearrangement is analogous to a Pinner reaction[9] (Scheme 2, path a).

Heating a solution of $\mathbf{2}\cdot BPh_4$ in CD_3CN to 65 °C for four hours in the presence of approximately one equivalent of NH_4PF_6 results in the formation of the trideuterated amide $[D_3]\mathbf{4}^{2+}$ via the trideuterated imino ester $[D_3]\mathbf{3}^{2+}$, as evident by ^{1}H NMR spectroscopy (Scheme 1). We obtained undeuterated $\mathbf{4}^{2+}$ as pure $\mathbf{4}\cdot(BPh_4)_2\cdot MeCN$ through the analogous reaction in MeCN, followed by addition of one equivalent of $NaBPh_4$ and partial evaporation of the solvent.

Opaque, colorless crystals of $\mathbf{4}\cdot(BPh_4)_2\cdot CH_3CN$ that were suitable for X-ray diffraction were obtained by the slow cooling of a hot, saturated solution of $\mathbf{4}\cdot(BPh_4)_2$ in CH_3CN. The crystal structure of $\mathbf{4}^{2+}$ (Figure 1)[10] confirms the rearrangement of the N,C-coordinated 2-(acetimidoyloxy)ethyl group in $\mathbf{3}^{2+}$ to the O,C-coordinated 2-(acetylamino)ethyl group in $\mathbf{4}^{2+}$. Bond lengths observed for $\mathbf{4}^{2+}$ are comparable to those of other rhodium and iridium amide complexes.[11]

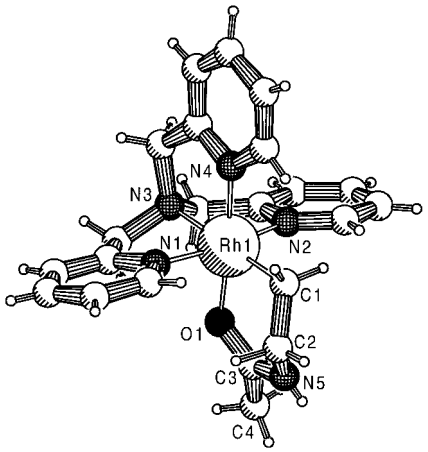
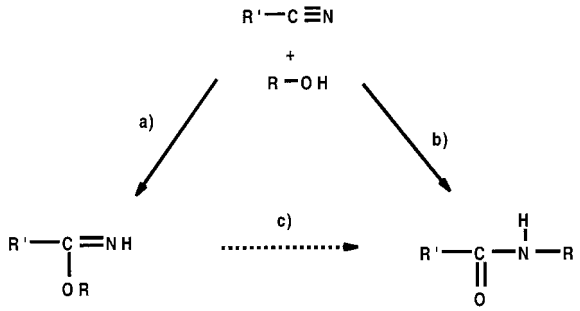


Figure 1. X-ray crystal structure of amide $\mathbf{4}^{2+}$. Selected bond lengths [Å] and angles [°]: Rh1 – N1 2.034(4), Rh1 – N2, 2.048(4), Rh1 – N3 2.142(3), Rh1 – N4 2.007(4), Rh1 – O1 2.051(3), Rh1 – C1 2.063(5), C1 – C2 1.496(9), C2 – N5 1.443(7), N5 – C3 1.319(6), O1 – C3 1.261(5), C3 – C4 1.487(6); O1-Rh1-C1 91.1(2), Rh1-C1-C2 111.7(4), C1-C2-N5 114.5(5), C2-N5-C3 124.9(5), N5-C3-O1 121.4(5), C3-O1-Rh1 126.8(3), C4-C3-O1 118.9(4), C4-C3-N5 119.7(5).

Heating a CD_3CN or [D$_6$]DMSO solution of a sample of pure $\mathbf{3}\cdot(BPh_4)_2\cdot MeOH$ to 65 °C resulted in quantitative rearrangement to $\mathbf{4}^{2+}$ within 3.5 hours. The lack of incorporation of CD_3CN upon rearrangement of $\mathbf{3}^{2+}$ to $\mathbf{4}^{2+}$ in CD_3CN demonstrates that the transformation is truly intramolecular. The rearrangement was found to be unaffected by the presence of up to ten mol H_2O per mol $\mathbf{3}^{2+}$ in both CD_3CN and [D$_6$]DMSO, which showed that imino ester $\mathbf{3}^{2+}$ and amide $\mathbf{4}^{2+}$ are both relatively stable towards hydrolysis.

The observed bands $\tilde{\nu}_{C=N}$ (1634 cm^{-1}) for $\mathbf{3}^{2+}$ and $\tilde{\nu}_{C=O}$ (1600 cm^{-1}) for $\mathbf{4}^{2+}$ are in accordance with their crystal structure. Selected NMR data for the $RhCH_2CH_2O$ fragment of $\mathbf{2}^{+}$, the $RhCH_2CH_2OC(Me)$=NH fragment of $\mathbf{3}^{2+}$, and the $RhCH_2CH_2NHC(Me)$=O fragment of $\mathbf{4}^{2+}$ are summarized in Table 1. The significant up-field shifts in the ^{1}H and ^{13}C NMR spectra of the CH_2N fragment in $\mathbf{4}^{2+}$ relative to the CH_2O fragment in $\mathbf{2}^{+}$ and $\mathbf{3}^{2+}$ are diagnostic of the conversion of $\mathbf{3}^{2+}$ to $\mathbf{4}^{2+}$.

The overall rearrangement of intermediate $\mathbf{2a}^{2+}$ to $\mathbf{4}^{2+}$ is analogous to the Ritter reaction[9] (Scheme 2, path b). To the best of our knowledge, the conversion of Pinner-type product $\mathbf{3}^{2+}$ into Ritter-type product $\mathbf{4}^{2+}$ is an unprecedented example of the rearrangement of an alkylalkanimidate to an *N*-alkylalkanamide (Scheme 2, path c: R,R′ = alkyl). The heating of alkylalkanimidates generally results in elimination of



Scheme 2. Reaction of alcohols with nitriles in acidic media. a) Formation of the imidate by Pinner addition; b) formation of amide by Ritter reaction; c) rearrangement of the imidate to an amide.

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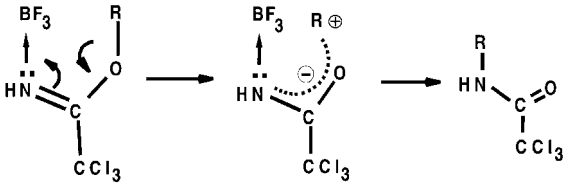
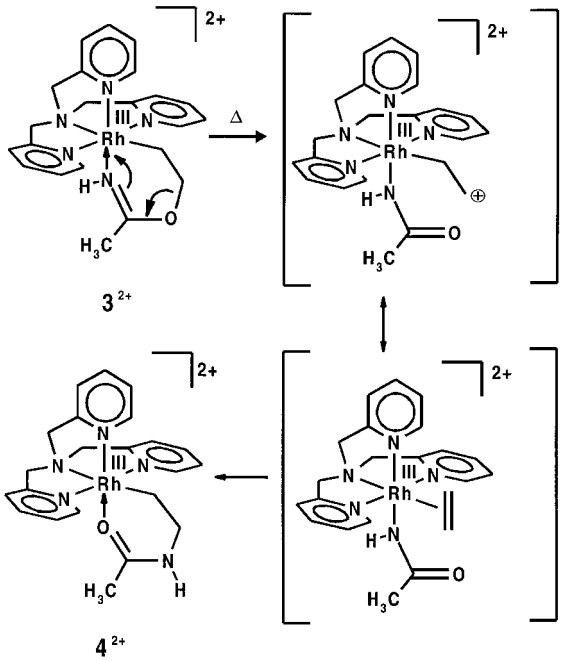
alcohols.[12] However, the BF_3-catalyzed rearrangement of alkyltrichloroacetimidates (Scheme 2, path c: R = alkyl, R′ = CCl_3) to *N*-alkyltrichloroacetamides has been reported.[13] The mechanism proposed for this reaction involves the formation of an alkyl cation–trichloroacetimidate ion pair (Scheme 3).



Scheme 3. Proposed mechanism for the BF_3-catalyzed rearrangement of alkyltrichloroacetimidates to *N*-alkyltricloroacetamides.[13]

We propose that the mechanism for the transformation of $\mathbf{3}^{2+}$ to $\mathbf{4}^{2+}$ proceeds via the route shown in Scheme 4. β-elimination of the acetimidato group gives an acetamidato–ethene complex, which then reacts through the migratory insertion of the ethene into the Rh–N bond.



Scheme 4. Proposed mechanism for the thermal rearrangement of $\mathbf{3}^{2+}$ to $\mathbf{4}^{2+}$.

The overall conversion of ethene complex $\mathbf{1}^{+}$ into a κ^2-*N*,*C*-2-(acetylamino)ethyl complex $\mathbf{4}^{2+}$ (Scheme 1) is the first example of a two-step amidation of a coordinated olefin by H_2O_2 and H^+/MeCN. The synthetic applicability of this reaction is currently under investigation.

Experimental Section

$\mathbf{3}\cdot(BPh_4)_2$: NH_4PF_6 (25 mg, 0.15 mmol) was added to a solution of $\mathbf{2}\cdot BPh_4$ (100 mg, 0.13 mmol) in CH_3CN (10 mL), and the solution stirred at room temperature for 4 hours. Subsequently, a solution of $NaBPh_4$ (45 mg, 0.13 mmol) in CH_3CN (5 mL) was added, and the solvent was partially evaporated under vacuum to about 5 mL. Compound $\mathbf{3}\cdot(BPh_4)_2\cdot 1.5\,H_2O$ was precipitated as a white powder by adding MeOH (ca. 10 mL). Opaque colorless crystals of $\mathbf{3}\cdot(BPh_4)_2\cdot MeOH$ were obtained by slow crystallization of the above powder from DMSO/MeOH at $-10\,^{\circ}C$. Yield: 131 mg (88 %). The presence of approximately 1.5 mol water and 1 mol MeOH per mol $\mathbf{3}^{2+}$ in the powder and the crystals, respectively, was confirmed by ^1H NMR spectroscopy. ^1H NMR (200.13 MHz, CD_3CN, 298 K): $\delta = 8.70$ (d, 1H, $^3J(H,H) = 5.6$ Hz; Py_a-H6), 8.32 (d, 2H, $^3J(H,H) = 5.9$ Hz; Py_b-H6), 8.0–6.8 (m, 9H; py-H4, -H5, and -H3), 7.31 (m, 8H; BAr-H2), 7.03 (t, 8H, $^3J(H,H) = 7.3$ Hz; BAr-H3), 6.87 (t, 4H, $^3J(H,H) = 7.3$ Hz; BAr-H4), 5.48 (d[AB], 2H; $^3J(H,H) = 16.8$ Hz; NCH_2-Py_b), 5.08 (d[AB], 2H, $^3J(H,H) = 16.8$ Hz; NCH_2-Py_b), 4.84 (s, 2H; NCH_2-Py_a), 4.26 (t, 2H, $^3J(H,H) = 5.6$ Hz; $RhCH_2CH_2O$), 3.38 (dt, 2H, $^3J(H,H) = 5.6$ Hz, $^2J(H,Rh) = 2.7$ Hz; $RhCH_2CH_2O$), 2.11 (s, 3H; OC(CH_3)=N); the ^1H NMR spectrum in [D_6]DMSO shows an additional signal at $\delta = 8.35$ (br s, 1H, NH); $^{13}C\{^1H\}$ NMR (50.33 MHz, [D_6]DMSO, 298 K): $\delta = 179.5$ (OC(CH_3)=N), 164.3 (Py_b-C2), 163.2 (Py_a-C2), 163.4 (q, $^1J(C,B) = 48.6$ Hz; BAr-C1), 150.2 (Py_b-C6), 148.8 (Py_a-C6), 140.1 (Py_b-C4), 139.5 (Py_a-C4), 135.6 (BAr-C2), 126.0 (Py_b-C3), 125.3 (q, $^3J(C,B) = 2.8$ Hz; BAr-C3, Py_a-C3), 124.9 (Py_b-C5), 122.3 (Py_a-C5), 121.6 (BAr-C4) 71.8 ($RhCH_2CH_2O$), 65.6 (N-CH_2-Py_a), 64.9 (NCH_2-Py_b), 28.4 (d, $^1J(C,Rh) = 26.4$ Hz, $RhCH_2CH_2O$), 21.6 (OC(CH_3)=N); FT-IR (KBr): $\tilde{\nu} = 3605$ (m), 3509 (m), 3275 (m), 1634 cm^{-1} (s, C=N); FAB-MS (*m*-nitrobenzylalcohol (Noba)/CH_3CN): *m/z*: 798 [$M - BPh_4$]$^+$, 478 [$M - H - (BPh_4)_2$]$^+$, 393 [$M - (CH_2CH_2OC(CH_3)$=NH) – $(BPh_4)_2$+H]$^+$; FAB-MS (*m*-Noba/CH_3CN) from a sample prepared from a CD_3CN solution: *m/z*: 801 [$M - BPh_4$]$^+$, 481 [$M - H - (BPh_4)_2$]$^+$, 393 [$M - (CH_2CH_2OC(CD_3)$=NH) – $(BPh_4)_2$+H]$^+$; elemental analysis calculated for $\mathbf{3}\cdot(BPh_4)_2\cdot 1.5\,H_2O$ ($C_{70}H_{69}N_5O_{2.5}B_2Rh$): C 73.44, H 6.07, N 6.12; found: C 73.50, H 6.32, N 6.02; calculated for $\mathbf{3}\cdot(BPh_4)_2\cdot MeOH$ ($C_{71}H_{70}N_5O_2B_2Rh$): C 74.16, H 6.14, N 6.09; found: C 74.30, H 6.09, N 6.41.

$\mathbf{4}\cdot(BPh_4)_2$: NH_4PF_6 (45 mg, 0.28 mmol) was added to a solution of $\mathbf{2}\cdot BPh_4$ (100 mg, 0.13 mmol) in CH_3CN (10 mL), and the solution heated to 65 °C for 4 h. Subsequently a solution of $NaBPh_4$ (90 mg, 0.26 mmol) in CH_3CN (5 mL) was added, and the solvent was partially evaporated under vacuum to about 3 mL. The solution was again heated to 65 °C and allowed to cool slowly to room temperature, which resulted in the slow crystallization of $\mathbf{4}\cdot(BPh_4)_2\cdot CH_3CN$ as opaque colorless crystals that were suitable for X-ray diffraction studies. Yield: 107 mg (71 %). ^1H NMR (200.13 MHz, CD_3CN, 298 K): $\delta = 8.59$ (d, 1H, $^3J(H,H) = 6.2$ Hz; Py_a-H6), 8.43 (d, 2H, $^3J(H,H) = 5.9$ Hz; Py_b-H6), 8.0–6.8 (m, 9H; py-H4, -H5, and -H3), 7.31 (m, 8H; BAr-H2), 7.03 (t, 8H, $^3J(H,H) = 7.3$ Hz; BAr-H3), 6.87 (t, 4H, $^3J(H,H) = 7.3$ Hz; BAr-H4), 5.45 (d[AB], 2H, $^3J(H,H) = 15.9$ Hz; NCH_2-Py_b), 5.07 (d[AB], 2H, $^3J(H,H) = 15.9$ Hz; NCH_2-Py_b), 4.94 (s, 2H; NCH_2-Py_a), 3.47 (dt, 2H, $^3J(H,H) = 5.9$ Hz, $^3J(Rh,H) = 2.4$ Hz; $RhCH_2CH_2NH$), 3.23 (t, 2H, $^3J(H,H) = 5.9$ Hz; $RhCH_2CH_2NH$), 1.80 (s, 3H, NHC(CH_3)=O); the ^1H NMR spectrum in [D_6]DMSO shows an additional signal at $\delta = 9.81$ (br s, 1H, NH); $^{13}C\{^1H\}$ NMR (50.33 MHz, [D_6]DMSO, 298 K): $\delta = 178.8$ (NHC(CH_3)=O), 164.9 (Py_b-C2), 164.3 (Py_a-C2), 163.4 (q, $^1J(C,B) = 48.6$ Hz; BAr-C1), 150.7 (Py_a-C6), 150.4 (Py_b-C6), 140.3 (Py_b-C4), 139.4 (Py_a-C4), 135.6 (BAr-C2), 125.9 (Py_b-C3), 125.3 (q, $^3J(C,B) = 2.8$ Hz; BAr-C3, Py_a-C3), 124.8 (Py_b-C5), 122.5 (Py_a-C5), 121.6 (BAr-C4), 65.4 (NCH_2-Py_b), 63.9 (NCH_2-Py_a), 41.5 ($RhCH_2CH_2NH$), 33.3 (d, $^1J(C,Rh) = 27.7$ Hz, $RhCH_2CH_2NH$), 21.5 (NHC(CH_3)=O); FT-IR (KBr): $\tilde{\nu} = 3307$ (s, NH), 1600 cm^{-1} (s, C=O); FAB-MS (*m*-Noba/CH_3CN): *m/z*: 798 [$M - BPh_4$]$^+$, 478 [$M - H - (BPh_4)_2$]$^+$, 393 [$M - (CH_2CH_2NHC(CH_3)$=O) – $(BPh_4)_2$+H]$^+$; elemental analysis calculated for $\mathbf{4}\cdot(BPh_4)_2\cdot CH_3CN$, ($C_{72}H_{69}N_6ORhB_2$): C 74.62, H 6.00, N 7.25; found: C 74.68, H 6.50, N 7.21.

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[1] a) D. M. Roundhill, *Chem. Rev.* **1992**, *29*, 1; b) D. M. Roundhill, *Catal. Today* **1997**, *37*, 155; c) J. J. Brunet, *Gazz. Chim. Ital.* **1997**, *127*, 111.
[2] a) M. Beller, M. Eichberger, H. Trauthwein, *Angew. Chem.* **1997**, *109*, 2306; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2225; b) J. J. Brunet, G. Commenges, D. Neibecker, K. Philippot, *J. Organomet. Chem.* **1994**,

  1433-7851/99/3801-0221 $ 17.50+.50/0

469, 221; c) A. L. Casalnuovo, J. C. Calabresse, D. Milstein, J. Am. Chem. Soc. **1988**, *110*, 6738; d) R. Dorta, P. Egli, F. Zürcher, A. Togni, *J. Am. Chem. Soc.* **1997**, *119*, 10857; e) M. A. Giardello, V. P. Conticello, L. Bard, M. R. Gagné, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10241; f) Y. Li, T. J. Marks, J. Am. Chem. Soc. **1996**, *118*, 9295; g) Y. Li, T. J. Marks, *Organometallics* **1996**, *15*, 3770; h) A. L. Seligson, W. C. Trogler, *Organometallics* **1993**, *12*, 744, and references therein.

[3] B. de Bruin, M. J. Boerakker, J. J. J. M. Donners, B. E. C. Christiaans, P. P. J. Schlebos, R. de Gelder, J. J. M. Smits, A. L. Spek, A. W. Gal, *Angew. Chem.* **1997**, 109, 2153; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2064.

[4] The few isolated 2-metallaoxetanes known are all stabilized by various substituents. Consequently, it is difficult to deduce the intrinsic reactivity of the unsubstituted 2-metallaoxetane moiety from these substituted examples: a) V. W. Day, W. G. Klemperer, S. P. Lockledge, D. J. Main, *J. Am. Chem. Soc.* **1990**, *112*, 2031; b) A. A. Zlota, F. Frolow, D. Milstein, *J. Am. Chem. Soc.* **1990**, *112*, 6411; c) M. J. Calhorda, A. M. Galvão, C. Ünaleroglu, A. A. Zlota, F. Frolow, D. Milstein, *Organometallics* **1993**, *12*, 3316; d) D. P. Klein, J. C. Hayes, R. G. Bergman, *J. Am. Chem. Soc.* **1988**, *110*, 3704; e) J. C. Hartwig, R. G. Bergman, R. A. Andersen, *Organometallics* **1991**, *10*, 3344; f) J. C. Hartwig, R. G. Bergman, R. A. Andersen, *J. Am. Chem. Soc.* **1990**, *112*, 3234; g) S. Baba, T. Ogura, S. Kawaguchi, H. Tokunan, Y. Kai, N. Kashi, *J. Chem. Soc. Chem. Commun.* **1972**, 910; h) L. Pandolfo, G. Paiaro, G. Valle, P. Ganis, *Gazz. Chim. Ital.* **1985**, *115*, 65; i) W. A. Herrmann, U. Küsthardt, A. Schäfer, E. Herdtweck, *Angew. Chem.* **1986**, *98*, 818; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 817; j) R. Schlodder, J. A. Ibers, M. Lenarda, M. Graziani, *J. Am. Chem. Soc.* **1974**, *96*, 6893; k) M. Lenarda, N. B. Pahor, M. Calligaris, M. Graziani, L. Randaccio, *J. Chem. Soc. Dalton Trans.* **1978**, 279.

[5] For an overview of 2-metallaoxetane reactivity, see K. A. Jørgensen, B. Schiøtt, *Chem. Rev.* **1990**, *90*, 1483.

[6] Details of the crystal structure determination are available as supporting information on the WWW.

[7] $\delta(CD_3CN) = 4.02$ (t, $^3J(H,H) = 7.4$ Hz; $RhCH_2CH_2O$), 3.27 (dt, $^3J(H,H) = 7.4$ Hz, $^2J(Rh,H) = 2.7$ Hz; $RhCH_2CH_2O$). These signals are similar to those recorded for separately prepared $[(tpa)Rh^{III}(2\text{-hydroxyethyl})(Cl)]BPh_4$: $\delta(CD_3CN) = 3.98$ (t, $^3J(H,H) = 7.9$ Hz; $RhCH_2CH_2O$), 3.16 (dt, $^3J(H,H) = 7.9$ Hz, $^2J(Rh,H) = 2.6$ Hz; $RhCH_2CH_2O$.

[8] For the intramolecular Pinner reaction from $[(PMe_3)_4Ir^{III}(CH_2OH)(N{\equiv}CMe)]^{2+}$ to κ^2-*N*,*C*-2-(acetimidoyloxy)-methyl complex $[(PMe_3)_4Ir^{III}(CH_2OC(Me){=}NH)]^{2+}$, see D. L. Thorn, J. C. Calabrese, *J. Organomet. Chem.* **1984**, *272*, 283. For other examples of nitrile C≡N-bond activation by metal coordination (including Pinner type reactions with alcohols), see B. N. Storhoff, H. C. Lewis Jr., *Coord. Chem. Rev.* **1977**, *23*, 1

[9] For the Pinner syntheses, see J. March, *Advanced Organic Chemistry*, 4th ed, Wiley, **1992**, p. 892, and references therein. For the Ritter reaction, see J. March, *Advanced Organic Chemistry*, 4th ed, Wiley, **1992**, p. 970, and references therein.

[10] Single crystals of $\mathbf{4}\cdot(BPh_4)_2\cdot CH_3CN$ were mounted in air on a glass fibre. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer with graphite monochromatized $Cu_{K\alpha}$ radiation ($\lambda = 1.541838$ Å). Data were collected at room temperature (θ–2θ scan mode). Unit cell dimensions were determined from the angular setting of 15 reflections. Intensity data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction (ψ scan)[10a] was applied. The structures were solved by the program system DIRDIF[10b] by using the program PATTY[10c] to locate the heavy atom and were refined with standard methods (refinement against F^2 of all reflections with SHELXL97[10d] with anisotropic parameters for the non-hydrogen atoms. The hydrogen atoms of the methyl groups were refined as rigid rotors with idealized sp^3 hybridization and a C–H bond length of 0.97 Å to match the maximum electron density in a difference Fourier map. The hydrogen atom attached to the nitrogen atom was taken from a difference Fourier map. All other hydrogen atoms were initially placed at calculated positions and were freely refined subsequently. Crystal data ($C_{72}H_{69}B_2N_6ORh$, $M_r = 1158.86$): monoclinic, space group $C2/c$, $a = 28.270(2)$, $b = 23.0952(14)$, $c = 21.520(2)$ Å, $\beta = 119.793(6)^\circ$, $V = 12192.9(16)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.263$ g cm^{-3}; final R indices: $R_1 = 0.0552$ (for 6778 reflections considered observed ($I > 2\sigma(I)$)), $wR_2 = 0.1255$ (all data) for the 993 total variables.[10e] a) A. C. T North, D. C. Philips, F. S. Mathews; *Acta Crystallogr.* **1968**, *A24*, 351; b) P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, DIRDIF-96, computer program system for crystal structure determination by Patterson and direct methods applied to difference-structure factors, Crystallography Laboratory, University of Nijmegen (Netherlands), **1996**; c) P. T. Beurskens, G. Beurskens, M. Strumpel, C. E. Nordman in *Patterson and Pattersons* (Eds.: J. P. Glusker, B. K. Patterson, M. Rossi), Clarendon, Oxford, **1987**, p. 356; d) G. M. Sheldrick, SHELXL-97, program for the refinement of crystal structures, Universität Göttingen (Germany), **1997**; e) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101855 and CCDC-101856 for $\mathbf{4}\cdot(BPh_4)_2\cdot$MeCN and $\mathbf{3}\cdot(BPh_4)_2\cdot$MeOH, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

[11] a) O Heilmann, H. D. Hausen, W. Kaim, *Z. Naturforsch Teil B* **1994**, *49*, 1554; b) B. McCullogh, J. Halpern, M. R. Thompson, C. R. Landis, *Organometallics* **1990**, *9*, 1392; c) M. Costa, G. P. Chiusoli, F. Salvadori, G. Bocelli, *Gazz. Chim. Ital* **1995**, *125*, 589; d) B. E. Villarroya, L. A. Oro, F. J. Lahoz, A. J. Edwards, M. A. Ciriano, P. A. Alonso, A. Tiripicchio, M. Tiripicchio Camellini, *Inorg. Chim. Acta* **1996**, *250*, 241; e) M. I. Arriortua, J. L. Pizarro, J. Ruiz, J. M. Morena, E. Colacio, *Inorg. Chim. Acta* **1995**, *231*, 103; f) G. Bocelli, G. P. Chiusoli, M. Costa, M. Michelotti, *J. Chem. Soc. Perkin Trans. 1* **1994**, 1347; g) N. W. Alcock, J. M. Brown, P. J. Maddox, *J. Chem. Soc. Chem. Comm.* **1986**, 1532; g) N. W. Alcock, J. M. Brown, A. E. Derome, A. R. Lucy, *J. Chem. Soc. Chem. Comm.* **1985**, 575.

[12] The thermal decomposition of alkylalkanimidates yields, among others, nitriles and alcohols or trisubstituted 1.3.5-triazines and alcohols: a) F. Cramer, K. Pawelzik, J. Kupper, *Angew. Chem.* **1956**, *20*, 649; b) P. Reynaud, R. C. Moreau, *Bull. Soc. Chim. Fr.* **1964**, 2997. See also ref. [13].

[13] F. Cramer, N. Hennrich, *Chem. Ber.* **1961**, 976, and references therein.

Domino Effect in the Buildup of N-I-N-I Chains of the *N*-Iodine(triphenylphosphane)imine

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Nitrogen–iodine compounds are often associated through N-I-N-I chains of the donor–acceptor type. Examples are the iodine–nitrogen derivatives $NI_3\cdot NH_3$[1] and $NI_3\cdot$pyridine,[2] which form polymers, and the iodine azide which is monomeric in the gas phase[3, 4] but forms zigzag chains with the iodine atoms in the solid state through the α-N atoms of the azide groups.[3] The hypervalent character of the iodine atoms in these compounds, which causes the association, reveals itself above all in the ionic derivatives $[I_2N_3]^+[SbF_6]^-$,[5] $[PPh_4]^+[I(N_3)_2]^-$,[6] and in the halide complexes of *N*-iodosuc-

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