ORGANOMETALLICS
Article

Organometallics **2009,** *28,* 5333–5340 5333
DOI: 10.1021/om9003412

Reactivity of Cationic Dinitrosyl Bisphosphine Rhenium Complexes toward Acetylene: Base-Controlled Product Formation

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Received April 30, 2009

Reactions of the dinitrosyl bisphosphine rhenium cations $[Re(NO)_2(PR_3)_2][BAr^F{}_4]$ (R = Cy **1a**; R = *i*Pr **1b**; $[BAr^F{}_4]^-$ = tetrakis[(3,5-bis(trifluoromethyl)phenyl)borate]) with acetylene yielded the alkynyl (*o*-vinyl)hydroxylamido nitrosyl bisphosphine complexes $[Re(CH{=}C(H)ONH)(C{\equiv}CH)(NO)(PR_3)_2][BAr^F{}_4]$ (**3a** and **3b**) in the absence of base, while in the presence of 2,6-di(*tert*-butyl)pyridine formation of the neutral alkynyl complexes $[Re(C{\equiv}CH)(NO)_2(PR_3)_2]$ (**4a** and **4b**) was observed. A plausible mechanism is presented and supported by various NMR techniques, IR spectroscopy, and DFT calculations. Treatment of **4a** and **4b** with $[H(OEt_2)_2][BAr^F{}_4]$ gave the corresponding vinylidene complexes $[Re(C{=}CH_2)(NO)_2(PR_3)_2][BAr^F{}_4]$ (**5a** and **5b**) in high yields, which only slowly convert into the alkynyl(*o*-vinyl)hydroxylamido nitrosyl bisphosphine complexes **3a** and **3b** when treated with a large excess of acetylene. Thiophenol or benzeneselenol underwent 1,2-additions onto the vinylidene ligands of **5a** and **5b** to yield the cationic Fischer-type carbene complexes $[Re(C(XPh)CH_3)(NO)_2(PR_3)_2][BAr^F{}_4]$ (X = S **6a**,**b**; X = Se **7a**,**b**) quantitatively. X-ray diffraction studies were carried out on **4b**, **5b**, and **7a**.

Introduction

The transition metal catalyzed olefin metathesis is nowadays one of the most widely used organic transformations.[1−4] Despite the fact that heterogeneous rhenium olefin metathesis catalysts are superior over their molybdenum- or tungsten-based analogues, defined soluble rhenium metathesis systems have rarely been found to show high catalytic activity.[5] The only catalyst precursors with rhenium in low oxidation states are the recently reported cationic dinitrosyl bisphosphine rhenium(−I) complexes $[Re(NO)_2(PR_3)_2][BAr^F{}_4]$ (R = Cy **1a**; R = *i*Pr **1b**; $[BAr^F{}_4]^-$ = tetrakis[(3,5-bis(trifluoromethyl)phenyl)borate]) and dinuclear rhenium carbonyl compounds.[6−8] Whereas **1a** and **1b** possess catalytic activity in ROMP processes, their benzylidene derivatives $[Re(=CHPh)(NO)_2(PR_3)_2][BAr^F{}_4]$ (R = Cy and *i*Pr) were found to be inactive in olefin metathesis reactions, presumably due to their insufficient initiation properties of the catalyses. Since low-valent dinitrosyl bisphosphine complexes of molybdenum and tungsten were reported to efficiently promote olefin metathesis reactions,[9,10] it was anticipated that their rhenium analogues with the general formula $[Re(alkylidene)(NO)_2(PR_3)_2]^+$ might principally be catalytically active as well. On the basis that the electrophilic character of dinitrosyl rhenium complexes' alkylidene ligands with reduced π-accepting properties seemed to be also appropriate, we probed Fischer-carbene rhenium complexes.[8,11,12]

Synthetic access to Fischer-type rhenium carbene complexes was based on acetylene or acetylide complexes with

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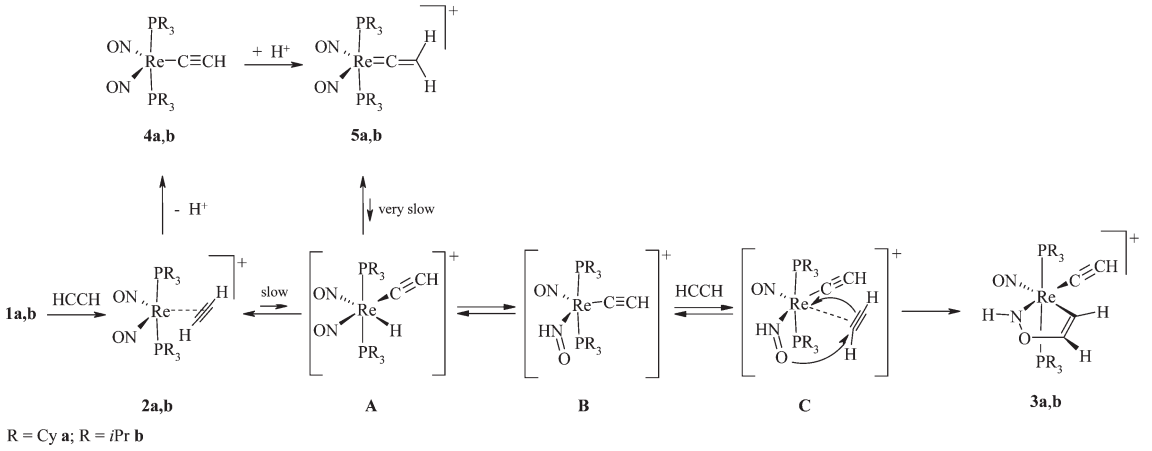
(1) Ivin, K. J.; Mol, J. C. In *Olefin Metathesis and Metathesis Polymerization*; Ivin, K. J., Mol, J. C., Eds.; Academic Press: San Diego, 1997.
(2) Zaragoza Dörwald, F. In *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999.
(3) Fürstner, A. *Angew. Chem.* **2000**, *112*, 3140; *Angew. Chem. Int. Ed.* 2000, 39, 3012.
(4) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2000**, *34*, 18.
(5) Chen, X.; Zhang, X.; Chen, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3798.
(6) (a) Herrmann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149. (b) Romao, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197. (c) Schrock, R. R.; Depue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (d) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844. (e) Weinstock, A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 135. (f) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448. (g) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 3367. (h) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127. (i) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Organomet. Chem.* **1996**, *520*, 69. (j) Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 2980. (k) LaPointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875.
(7) (a) Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1976**, *17*, 4251. (b) Doherty, M.; Siove, A.; Parlier, A.; Rudler, H.; Fontanille, M. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 33. (c) Warwel, S.; Siekermann, V. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 423.
(8) Frech, C. M.; Blacque, O.; Schmalle, H. W.; Berke, H.; Adlhart, C.; Chen, P. *Chem.—Eur. J.* **2006**, *12*, 3325.
(9) Zuech, E. A.; Hughes, W. B.; Kubicek, D. H.; Kittelman, E. T. *J. Am. Chem. Soc.* **1970**, *92*, 528.
(10) (a) Zuech, E. A. *J. Chem. Soc., Chem. Commun.* **1968**, 1182. (b) Taube, R.; Seyferth, K. *Z. Chem.* **1977**, *13*, 300. (c) Leconte, M.; Basset, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 7296. (d) Seyferth, K.; Rosenthal, K.; Kühn, G.; Taube, R. *Z. Anorg. Allg. Chem.* **1984**, *513*, 57. (e) Seyferth, K.; Taube, R. *J. Organomet. Chem.* **1984**, *262*, 191. (f) Keller, A.; Szterenberg, L. *J. Mol. Catal.* **1989**, *57*, 207. (g) Keller, A. *J. Organomet. Chem.* **1990**, *407*, 237. (h) Keller, A.; Szterenberg, L. *Z. Naturforsch.* **1991**, *47b*, 1469. (i) Keller, A. *J. Organomet. Chem.* **1992**, *436*, 199. (k) Keller, A. *J. Mol. Catal.* **1993**, *78*, L15.
(11) Frech, C. M.; Blacque, O.; Schmalle, H. W.; Berke, H. *Chem.—Eur. J.* **2006**, *12*, 5198.
(12) Jacobsen, H.; Heinze, K.; Llamazares, A.; Schmalle, H. W.; Artus, G.; Berke *J. Chem. Soc., Dalton Trans.* **1999**, 1717.

Published on Web 09/03/2009

Scheme 1



subsequent conversion into their vinylidene derivatives to enable 1,2-additions with protic nucleophiles, affording the desired alkylidene derivatives.

Results and Discussion

Synthesis of Alkynyl(*o*-vinyl)hydroxylamido Nitrosyl Bisphosphine Rhenium Complexes 3a and 3b. When benzene solutions of the cationic dinitrosyl bisphosphine rhenium complexes $[Re(NO)_2(PR_3)_2][BAr^F{}_4]$ (R = Cy **1a**; R = *i*Pr **1b**) were treated with acetylene at room temperature, the alkynyl(*o*-vinyl)hydroxylamido nitrosyl bisphosphine rhenium cations $[Re(C{\equiv}CH)(CH{=}C(H)ONH)(NO)(PR_3)_2][BAr^F{}_4]$ (**3a** and **3b**) precipitated from solution within 1 h, similar to the reported transformations of **1a** and **1b** with phenylacetylene.[13] A mechanistic path is expected to be initiated by coordination of acetylene on **1a** and **1b**. Indeed, when solutions of **1a** and **1b** in chlorobenzene-d_5 were treated with an excess of acetylene at −35 °C, an immediate color change occurred from dark red to yellow, indicating the initial formation of the acetylene adducts of type **2** (Scheme 1). These acetylene adducts (**2a** and **2b**) were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in solution. Their $^{31}P\{^1H\}$ NMR spectra showed singlets at δ = 16.2 and 24.1 ppm, while the ^1H NMR spectra in THF-d_8 exhibited broad triplets at δ ~7.8 ppm (J_{PH} = 3.7 Hz), which were assigned to the hydrogen atoms of the acetylene ligands. Subsequent formation of the acetylide hydride species **A** could lead to the prototropic nitroxyl acetylide intermediates of type **B**. These 16e$^-$ species **B** then coordinate another acetylene molecule to undergo a 1,3-dipolar addition of the ReN(H)O moiety via **C** and yield **3a** and **3b**.[14] Alternatively, **2a** and **2b** might be deprotonated to form the neutral acetylide complexes **4a** and **4b**. Treatment of methylene chloride solutions of **4a** and **4b** with equimolar amounts of $[H(Et_2O)_2][BAr^F{}_4]$ yielded the cationic vinylidene complexes **5a** and **5b** (see below). Protonation of the acetylide unit may be kinetically or thermodynamically determined. In fact, proton addition to the N_{NO} atom or the rhenium center was not observed. This latter observation contrasts the occurrence of **2a** and **2b** when starting from **1a** and **1b** and acetylene and therefore excludes that acetylide complexes of type **4** are involved in the reaction course to **3a** or **3b** (Scheme 1). **3a** and **3b** could be isolated as black solids in moderate yields (~50%). Slightly improved yields were obtained at prolonged reaction times; thus a ~60% yield of **3a** could be reached after three days and is accompanied by the formation of the cationic vinylidene complexes **5a** and **5b**, as indicated by NMR spectroscopy. However, the elemental analyses and the spectroscopic data of **3a** and **3b** were in agreement with the formation of the alkynyl(*o*-vinyl)hydroxylamido nitrosyl bisphosphine structures. For example, the $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b** revealed singlets at δ = 36.5 ppm and at δ = 43.0 ppm (THF-d_8), respectively. In the ^1H NMR spectra singlets were found at $\delta \approx 8.90$ ppm, which were attributed to the NH protons. The vinylic hydrogen atoms of the (*o*-vinyl)hydroxylamido moieties gave rise to signals at δ = 5.76 and 5.02 ppm and at δ = 5.69 and 5.26 ppm, respectively, whereas the acetylide protons appeared at δ = 4.34 and 4.41 ppm. Due to the low solubility of **3a** and **3b** in all common organic solvents and in water, $^{13}C\{^1H\}$ NMR spectra (or even 2D COSY NMR spectra) could not be obtained. The IR spectra exhibited characteristic absorptions at approximately 1720 cm^{-1} (ν_{NO}), 1600 cm^{-1} (ν_{HNO}), and 2090 cm^{-1} ($\nu_{C\equiv C}$) of both derivatives, consistent with the proposed structure of **3a** and **3b**.

Both reactions, that to the cationic dinitrosyl bisphosphine vinylidene complexes **5a** and **5b** and that to **3a** and **3b**, are thus assumed to pass through the acetylide hydride complexes of type **A** and are thought to be reversible at room temperature, however, with different rates. Reversibility of the reaction of the vinylidene complexes **5a** and **5b** with **A** is supported by the observation that when methylene chloride solutions were treated with an excess (~50 equiv) of acetylene gas, very slow formation of the alkynyl (*o*-vinyl)hydroxylamido nitrosyl bisphosphine complexes **3a** and **3b** was observed (10% conversion within three days).

DFT Calculations. Since the course of the reaction could not fully be unravelled spectroscopically with all its alternative pathways and intermediates, DFT calculations were sought using trimethylphosphine model complexes replacing P*i*Pr$_3$ and PCy$_3$ of the experimental systems. A plausible reaction path could be established relating **1-Me** and acetylene with **3-Me** in a strongly exothermic process (−70.1 kcal/mol) in the

(13) Frech, C. M.; Llamazares, A.; Alfonso, M.; Schmalle, H. W.; Berke, H. *Russ. Chem. Bull., Int. Ed.* **2004**, *53*, 1.

(14) (a) Werner, H.; Wolf, J.; Alonso, F. J.; Garcia; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397. (b) Hoehn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255. (c) Werner, H.; Hampp, A.; Peters, K.; Peters, E. M.; Walz, L.; Von Schnering, H.-G. *Z. Naturforsch., B: Chem. Sci.* **1990**, *45*, 1548. (d) Schaefer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *485*, 85. (e) Schaefer, M.; Wolf, J.; Werner, H. *Organometallics* **2004**, *23*, 5713.

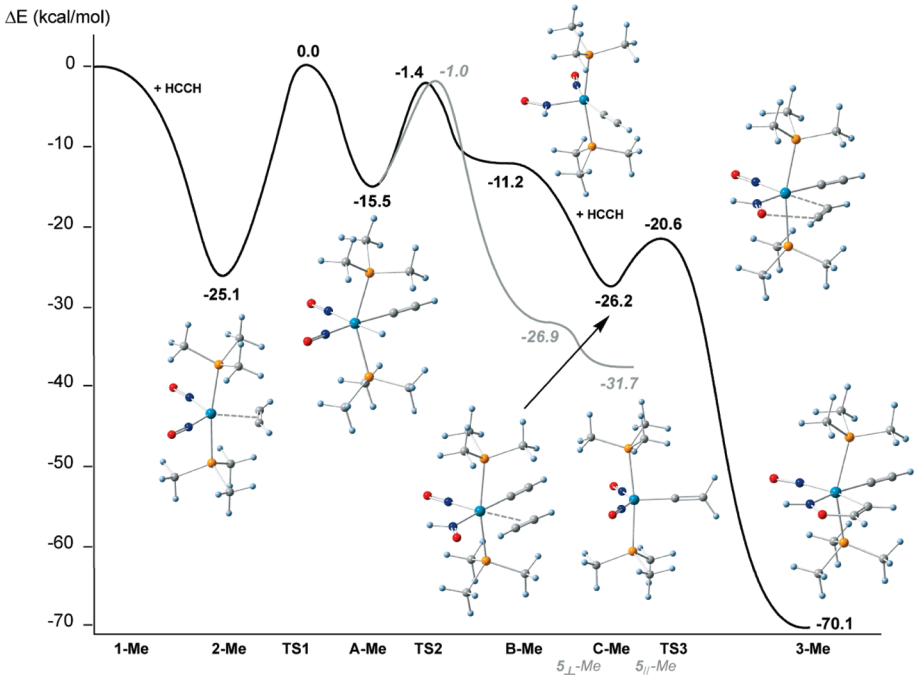


Figure 1. Energy diagram for calculated intermediates and transition states of the reaction of the cation **1-Me** with acetylene. Relative total energies are in kcal/mol with respect to those of **1-Me** and C_2H_2.

reaction with acetylene. The computed minimum energy pathways are presented in Figure 1.

Coordination of acetylene to the rhenium center of **1-Me** to form the acetylene complex **2-Me** is accompanied by a 25.1 kcal/mol stabilization. The η^2-coordinated acetylene orients itself perpendicular to the P−Re−P axis as expected for π acceptors in d^8 trigonal-bipyramidal structures.[15] Complex **3-Me** (in the presence of another acetylene molecule) is tremendously energetically greatly favored over **2-Me** by 45.0 kcal/mol, so that a gradual energetic descent to the product seems possible. The first step includes the formation of the hydride acetylide intermediate **A-Me**, which is endothermic by 9.6 kcal/mol with respect to **2-Me**. The optimized transition state **TS1**, which connects **2-Me** and **A-Me**, constitutes a relatively high reaction barrier of 25.1 kcal/mol. A dead-end track leads from **A-Me** to the vinylidene complex **5-Me**. The direct rearrangement of **2-Me** to **5-Me** via a 1,2-H shift could not be established by DFT. A reasonable pathway including a transition state could not be found on the given energy hypersurface. Starting from **A-Me**, migration of the H_{Re} atom was found to lead either to the nitroxyl intermediate **B-Me** or alternatively to the cationic vinylidene complex **5-Me**, since the calculated transition states are of very close in energy ($\Delta\Delta E_0^{\ddagger}$ = 0.4 kcal/mol). This result approximately matches with the experimentally observed product distribution of the vinylidene complexes **5** and the 3-rhena-2,3-dihydroisoxazoles **3**. It is noteworthy that the vinylidene unit of **5-Me** possesses somewhat hindered rotation with the prominent rotamer **5∥-Me**, where the vinylidene hydrogen atoms are parallel to the P−Re−P axis. The other rotamer **5⊥-Me**, with the vinylidene hydrogen atoms perpendicular to the P−Re−P axis, lies 4.8 kcal/mol higher in energy. The perpendicular rotamers seem to be very plausible intermediates reverting **5ab** to the hydride acetylide complexes **A-Me** on a least-motion pathway. The calculated total reaction barrier for this reverse reaction of 30.7 kcal/mol (**5∥-Me** → **A-Me**) is then split up in two parts, and the last big jump in energy is reduced by 4.8 kcal/mol. Nevertheless, the calculated residual reaction barrier of 25.9 kcal/mol is still relatively high. If it matches reality, we have to assume a very slow back-reaction, indeed in line with the experiments.[16] Addition of the second acetylene molecule to the $16e^-$ metal center of **B-Me** to form **C-Me** is calculated to be exothermic by −15.0 kcal/mol. The subsequent rearrangement of **C-Me** leading to **3-Me** can be interpreted in terms of a 1,3-dipolar addition with primary nucleophilic attack of O_{HNO} onto the acetylene ligand (see Figure 2). The process was calculated to be energetically highly favorable by 43.9 kcal/mol with a reaction barrier (**TS3**) of only 5.6 kcal/mol.

Summarizing the calculations, one could state that the crucial reaction barrier of the whole process from complexes of type **1** to those of type **3** is set by the transformation of the acetylene complexes **2** to hydride acetylide species **A**, and if the vinylidene species of type **5** are starting materials, they can be converted only by a still slower reaction.

Synthesis of Alkynyl Complexes 4a and 4b. The formation of **3a** and **3b** was suppressed when acetylene was added to benzene or chlorobenzene solutions of **1a** and **1b** at room temperature in the presence of a noncoordinating base such as 2,6-di(*tert*-butyl)pyridine. Apparently deprotonation of the acidic proton of the acetylene ligand of intermediates of type **A** promotes fast and clean conversions into the stable σ-alkynyl complexes $[Re(C{\equiv}CH)(NO)_2(PR_3)_2]$ **4a** and **4b**, which were isolated in good yields (~80%) as orange powders (Scheme 2). The type of added base, however, turned out to be crucial. When KO*t*Bu was used, significantly lower yields (~50%) of **4a** and **4b** and in addition precipitation of **3a** and **3b** were observed. This difference in the reaction

(15) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. In *Orbital Interactions in Chemistry*; John Wiley & Sons, Inc.: New York, 1984.

(16) The calculated reaction barrier difference of **5⊥-Me** → **A-Me** and **A-Me** → **B-Me** is 0.8 kcal/mol and compares well with the experimental observations.

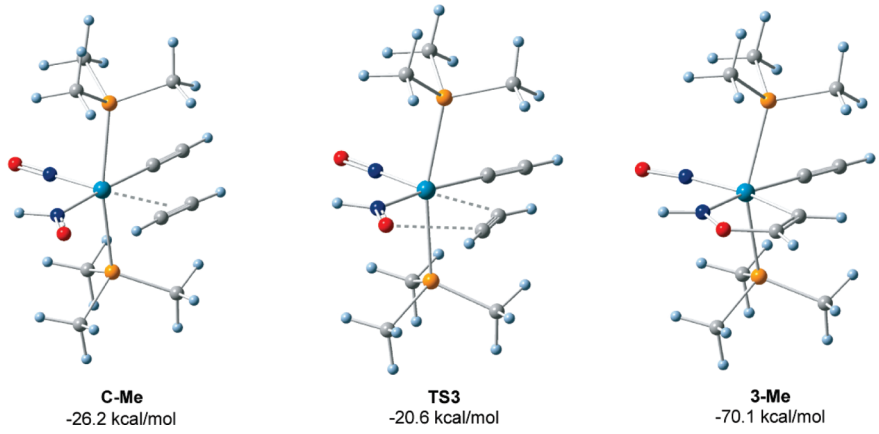
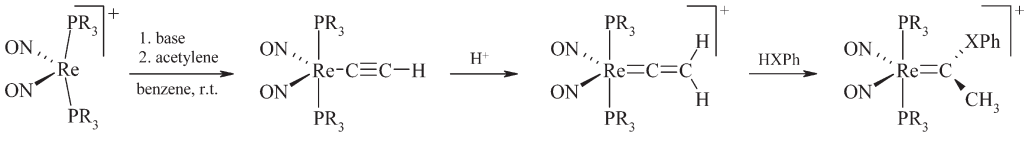


Figure 2. Views of optimized structures of various intermediates and a transition state. Values in kcal/mol represent the relative energies with respect to **1-Me** and two acetylenes.

Scheme 2



1a,b **4a,b** **5a,b** **6a,b** and **7a,b**

base = 2,6-di(*t*-butyl)pyridine

X = S **6**; X = Se **7**

R = Cy **a**; R = *i*Pr **b**

behavior was explained on the basis of a kinetically too slow base attack of the heterogeneous KO*t*Bu reagent. The $^{31}P\{^1H\}$ NMR spectra of both alkynyl complexes **4a** and **4b** exhibited singlet resonances at δ = 20.6 and 26.4 ppm in benzene solutions. The ^1H NMR spectra showed phosphine signals in addition to a broad poorly resolved triplet at δ = 4.14 ppm (J_{PH} = 3.9 Hz) for **4a** and a well-defined triplet at δ = 4.04 ppm (J_{PH} = 4.2 Hz) for **4b**, which were assigned to the hydrogen atoms of the alkynyl units. The $^{13}C\{^1H\}$ NMR spectra displayed triplets at δ = 111.9 and 111.7 ppm (J_{PC} = 19 and J_{PC} = 19 Hz) and at δ = 127.8 and 126.3 ppm (J_{PC} = 2 Hz for both) for the acetylenic carbon atoms. The latter resonances of the C_β atoms showed correlation with the signals of the alkynyl protons at δ = 4.14 ppm (**4a**) and at δ = 4.04 ppm (**4b**) in the 2D spectra. The IR spectra of **4a** and **4b** exhibited two characteristic ν(NO) absorptions at 1581 and 1621 cm^{-1} and at 1576 and 1618 cm^{-1}, respectively.

In order to further support the spectroscopically assigned structures of these alkynyl complexes, an exemplary X-ray diffraction study was carried out on single crystals of **4b** (Figure 5). Well-diffracting crystals were grown at −30 °C by slow diffusion of *n*-pentane into a concentrated toluene solution of **4b**. The solid state structure revealed the rhenium center in a pseudo-trigonal-bipyramidal environment (N1−Re1−N2 = 120.83(15)°, C1−Re1−N1 = 119.28(16)°, C1−Re1−N2 = 119.86(17)°) with the two phosphine ligands in axial positions. The P1−Re1−P2 angle is 164.07(3)° and both ligands hinge toward the acetylide ligand, as it was also observed in related systems.[12] The Re1−C1 and C1−C2 bond distances of **4b** are 2.127(4) and 1.182(6) Å and compare well with the bond distances of the recently reported alkynyl complex [(triphos)$(CO)_2$Re{C≡CC$(Ph)_2$(pyrazolyl)}], where Re−C and C−C bond distances of 2.118(5) and 1.203(8) Å were measured.[17] The hydrogen atom H1 was located in the difference Fourier map and refined isotropically. An ORTEP plot of the crystal structure of **4b** is presented in Figure 3. **4a** is a rare example of a rhenium alkynyl derivative analyzed by X-ray diffraction methods. The few crystallographically studied rhenium alkynyl complexes have the rhenium center in the oxidation state of +I, and most of them are cyclopentadienyl or carbonyl derivatives; their Re−C_α and C_α−C_β bond distances have been found to vary within a very large range.[18,19]

Synthesis of Vinylidene Complexes 5a and 5b. As mentioned above, equimolar amounts of the acid $[H(OEt_2)_2][BAr^F{}_4]$ can

(17) (a) Mantovani, N.; Bergamini, P.; Marchi, A.; Marvelli, L.; Rossi, R.; Bertolasi, V.; Ferretti, V.; De los Rios, I.; Peruzzini, M. *Organometallics* **2006**, *25*, 416. (b) Yam, V.; Lau, C.; Cheung, K.-K. *Organometallics* **1995**, *14*, 2749.

(18) See for instance: (a) Dembinski, R.; Lis, T.; Szafert, S.; Mayne, C. L.; Bartik, T.; Gladysz, J. A. *J. Organomet. Chem.* **1999**, *578*, 229. (b) Falloon, S. B.; Weng, W.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1997**, *16*, 2008. (c) Senn, D. R; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096. (d) Paul, F.; Meyer, W. E; Toupet, L.; Jiao, H.; Gladysz, J. A; Lapinte, C. *J. Am. Chem. Soc.* **2000**, *122*, 9405. (e) Weng, W.; Ramsden, J. A; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824.

(19) See for instance: (a) Lam, S. C.-F.; Yam, V. W.-W.; Wong, K. M.-C.; Cheng, E. C.-C.; Zhu, N. *Organometallics* **2005**, *24*, 4298. (b) Yam, V.W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1996**, *15*, 1740. (c) Chong, S. H.-F.; Lam, S. C.-F.; Yam, V. W.-W.; Zhu, N.; Cheung, K.-K. *Organometallics* **2004**, *23*, 4924. (d) Ferrer, M.; Rodriguez, L.; Rossell, O.; Lima, J. C.; Gomez-Sal, P.; Martin, A. *Organometallics* **2004**, *23*, 5096. (e) Yam, V. W.-W.; Chong, S. H.-F.; Ko, C.-C.; Cheung, K.-K. *Organometallics* **2000**, *19*, 5092. (f) Yam, V. W.-W.; Chong, S. H.-F.; Cheung, K.-K. *Chem. Commun.* **1998**, 2121. (g) Wong, K. M.-C.; Lam, S. C.-F.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W.; Roue, S.; Lapinte, C.; Fathallah, S.; Costuas, K.; Kahlal, S.; Halet, J.-F. *Inorg. Chem.* **2003**, *42*, 7086.

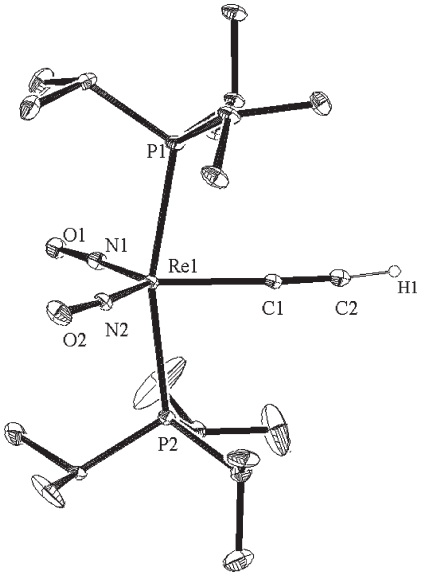


Figure 3. Molecular structure of **4b** with 20% probability displacement ellipsoids. All H atoms, except for H1, have been omitted for clarity. Selected bond distances (Å) and angles (deg): Re1−N1 = 1.788(3), Re−N2 = 1.790(3), Re1−C1 = 2.127(4), C1−C2 = 1.182(6), C2−H1 = 1.00(6). N1−O1 = 1.208(4), N2−O2 = 1.199(4), N1−Re1−N2 = 120.83(15), P1−Re1−P2 = 164.07(3), N1−Re1−C1 = 119.28(16), N2−Re1−C1 = 119.86(17), Re1−C1−C2 = 174.5(5), C1−C1−H1 = 175(4), Re1−N1−O1 = 171.0(3), Re1−N2−O2 = 172.5(3).

convert in methylene chloride the alkynyl complexes **4a** and **4b** into the olive green vinylidene complexes $[Re(CCH_2)(NO)_2(PR_3)_2][BAr^F{}_4]$ **5a** and **5b** with protonation at the C_β position. The $^{31}P\{^1H\}$ NMR spectra of **5a** and **5b** exhibit singlets at δ = 24.8 ppm and at δ = 31.9 ppm, respectively, and the ^1H NMR spectra displayed all resonances attributable to the phosphine ligands. The vinylidene protons appear as triplets. At δ = 5.82 ppm (J_{PH} = 2.3 Hz) one finds a unresolved triplet for **5a** and a well-defined triplet centered at δ = 5.57 ppm (J_{PH} = 2.8 Hz) for **5b**. The $^{13}C\{^1H\}$ NMR spectrum exhibits for the vinylidene unit of **5a** a broad signal at δ = 322.5 and a singlet at δ = 122.0 ppm and for **5b** a triplet at δ = 320.9 (J_{PC} = 15.4 Hz) and a singlet at δ = 121.3 ppm. The IR spectra display two characteristic ν(NO) absorptions at 1751 and 1652 cm^{-1} and one ν(C=C) absorption at 1612 cm^{-1} for **5a** and at 1753, 1650, and 1609 cm^{-1}, respectively, for **5b**. Due to the very different electronic properties of the vinylidene and the alkynyl residues (π acceptor vs predominantly π donor property) and the different charges of the complexes, the ν(NO) absorptions are shifted dramatically to higher wave numbers in comparison with those of **4a** and **4b**, for which absorptions at 1621 and 1581 cm^{-1} (**4a**) and at 1618 and 1576 cm^{-1} (**4b**) were found. ON−Re−NO angles of approximately 140° were calculated from the ν(NO) band intensities of **5a** and **5b**.[20] Crystals of **5b** suitable for X-ray diffraction were grown by slow evaporation of a concentrated methylene chloride solution. The determined molecular structure of **5b** is shown in Figure 4.

The rhenium center possesses approximate trigonal-bipyramidal coordination with the phosphine ligands in axial positions. The Re1−C1 and C1−C2 bond distances are 1.902(6) and 1.309(9) Å. Crystallographically characterized vinylidene complexes with rhenium centers are very rare. They normally display Re−C and C=C bond distances in the range 1.839−2.046 and 1.289−1.387 Å, respectively.[21] The N1−Re1−N2 angle of **5b** is 147.2(2)° and is significantly larger with respect to the one found in complex **4b** (N1−Re1−N2 = 120.83(15)°). As suggested by the DFT calculations on **5-Me**, the orientation of the vinylidene CH_2 plane is perpendicular to the trigonal plane of the trigonal bipyramid, which reflects the tendency to optimize the overlap with the "better" in-plane π donor orbital of d^8-C_{2v}-tetracoordinate metal fragments.

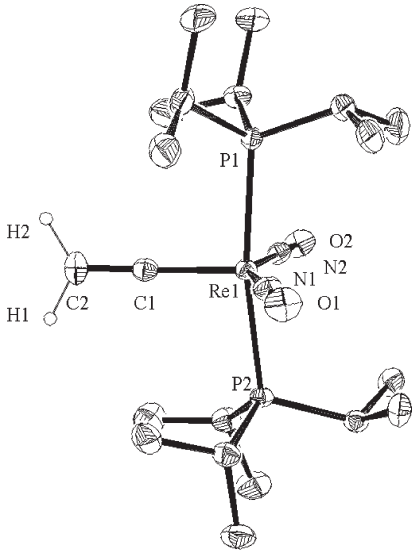


Figure 4. Molecular structure of **5b** with 30% probability displacement ellipsoids. The $[BAr^F{}_4]^-$ anion and all H atoms, except H1 and H2, have been omitted for clarity. Selected bond distances (Å) and angles (deg): Re1−N1 = 1.830(5), Re1−N2 = 1.827(5), Re1−C1 = 1.902(6), C1−C2 = 1.309(9), N1−O1 = 1.185(6), N2−O2 = 1.178(7), N1−Re1−N2 = 147.2(2), N1−Re1−C1 = 106.5(3), N2−Re1−C1 = 106.3(2), P1−Re1−P2 = 170.49(5).

Synthesis of Fischer-Carbene Complexes $[Re\{C(XPh)CH_3\}(NO)_2(PR_3)_2][BAr^F{}_4]$ (X = S 6a,b; X = Se 7a,b). When methylene chloride solutions of the vinylidene complexes **5a** and **5b** were treated with an excess (10 equiv) or an equimolar amount of thiophenol or benzoselenol, almost quantitative formation of Fischer-type carbene complexes $[Re\{C(XPh)CH_3\}(NO)_2(PR_3)_2][BAr^F{}_4]$ (X = S **6a**,**b**; X = Se **7a**,**b**) was observed. The reactions were over in a few seconds, accompanied by an immediate color change from olive green to dark violet. The $^{31}P\{^1H\}$ NMR spectra revealed unique singlets for all these compounds. The ^1H NMR spectra of these complexes showed not only signals for the phosphine ligands and the aryl residues but also resonances at $\delta \approx 3.4$ ppm, which were assigned to the methyl groups of the

(20) (a) Beck, W.; Melnikoff, A.; Stahl, R. *Chem. Ber.* **1966**, *99*, 3721. (b) Poletti, A.; Foffani, A.; Cataliotti, R. *Spectrochim. Acta* **1970**, *26A*, 1063.

(21) (a) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M.; Antipin, M. Y.; Struchkov, Y. T. *J. Organomet. Chem.* **1977**, *137*, 69. (b) Pombeiro, A. J. L.; Jeffrey, J. C.; Pickett, C. J.; Richards, R. L. *J. Organomet. Chem.* **1984**, *277*, C7. (c) Pombeiro, A. J. L.; Almeida, S. S. P. R.; Silva, M. F. C. G.; Jeffrey, J. C.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1989**, 2381. (d) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R. *Organometallics* **1996**, *15*, 3804. (e) Valyaev, D. A.; Semeikin, O. V.; Peterleitner, M. G.; Borisov, Y. A.; Khrustalev, V. N.; Mazhuga, A. M.; Kremer, E. V.; Ustynyuk, N. A. *J. Organomet. Chem.* **2004**, *689*, 3837.

carbene moieties. In the $^{13}C\{^1H\}$ NMR spectra resonances were found with approximate chemical shifts of $\delta \approx 305$ ppm, which are characteristic for the $C_{carbene}$ atoms. In the case of the triisopropyl derivatives **6b** and **7b** these signals appeared as well-defined triplets ($J_{PC} = 3.5$ Hz), but as broad resonances with unresolved couplings in the case of the tricyclohexyl species **6a** and **7a**.

It was expected that the carbene ligands of **6a**,**b** and **7a**,**b** would have significantly smaller ON−Re−NO angles than those reported for their benzylidene derivatives $[Re(=CHPh)(NO)_2(PR_3)_2][BAr^F_4]$.[8] As a consequence, larger P−Re−P angles and elongated Re−C bond distances were predicted.[12] Indeed, the calculations of the angles from the ν(NO) IR intensities of **6a** and **6b** and those of **7a** and **7b** resulted in angles of approximately 140°,[20] which compare well with the ones determined for the vinylidene complexes **5a** and **5b**. An exemplary X-ray diffraction study on **7a** confirmed this (Figure 5). Single crystals of **7a** were grown by slow evaporation of concentrated diisopropylether solutions at −30 °C.

In the solid state **7a** revealed a pseudo-trigonal-bipyramidal coordination at the rhenium center (Figure 5). In accord with the IR-derived data the N1−Re1−N2 angle is 146.69(14)° and compares well to the respective one of **5b** (N1−Re1−N2 = 147.2(2)°). In contrast to this, the P−Re−P angles differ significantly (P1−Re1−P2 = 163.63(4)° (**7a**) vs P1−Re1−P2 = 170.49(5)° (**5b**)). The Re−C1 bond distance of **7a** is 1.994(5) Å. Due to the reduced π-accepting properties of the Fischer-carbenes, the $Re-C_{carbene}$ bond distance in **7a** (1.994(5) Å) is elongated by 0.092, 0.037, and 0.027 Å in comparison with the $Re-C_{vinylidene}$ bond length in **5b** (1.902(6) Å) and the $Re-C_{benzylidene}$ bond lengths in $[Re(=CHPh)(NO)_2(PiPr_3)_2][BAr^F_4]$ (1.957(3) Å) and $[Re(=CHPh)(NO)_2(PCy_3)_2][BAr^F_4]$ (1.967(7) Å), respectively.[8,22] Moreover, the reduced electrophilicity of the Fischer-carbene units in **6a**,**b** and **7a**,**b** causes smaller No−Re−NO angles, which leads to a higher stability when compared to the benzylidene complexes $[Re(=CHPh)(NO)_2(PR_3)_2][BAr^F_4]$ (R = Cy and *i*Pr). For instance, electrophilicity of the $C_{carbene}$ atoms of the latter induces phosphine migration onto this atom at elevated temperatures.[8] Other reaction patterns such as the acetonitrile-promoted alkylidene migration onto a nitrosyl ligand and nitrosyl oxidation were also absent for **6a**,**b** and **7a**,**b**.[11,22,24] Similarly, no catalytic activity was observed when norbornene ROMP was attempted (under various reaction conditions) with **6a**,**b** or **7a**,**b**, which imlies that alkylidene complexes based on the $[Re(PR_3)_2(NO)_2]^+$ framework are not suitable to promote olefin metathesis reactions.[11,23]

Conclusion

Reactions of the $[Re(NO)_2(PR_3)_2]^+$ cations (R = Cy **1a**; R = *i*Pr **1b**) with acetylene under various chemical conditions are described. For instance, treatment of **1a** and **1b** with acetylene in the absence of a base yielded the alkynyl(*o*-vinyl)hydroxylamido nitrosyl bisphosphine complexes $[Re(C\equiv CH)\{CH=C(H)ONH\}(NO)(PR_3)_2][BAr^F_4]$ (**3a** and **3b**), while the neutral alkynyl complexes of type **4** were formed in the presence of a base. A plausible reaction mechanism for the conversion of the complexes of type **1** into those of type **3** was elaborated on the basis of experimental observations and DFT calculations. Primary formation of acetylene complexes allows access of hydride acetylide compounds with H migration. These complexes in turn undergo further H migration to form nitroxyl compounds, which take up another acetylene molecule. 1,3-Dipolar addition of the acetylene to the nitroxyl rhenium moiety furnishes type **3** complexes. Protonation of the alkynyl complexes exclusively yielded the cationic vinylidene species **5a** and **5b**, which undergo 1,2-additions with protic nucleophiles to yield the Fischer-carbene complexes **6a**,**b** and **7a**,**b**. It was found that rhenium dinitrosyl bisphosphine Fischer-carbene complexes are not suitable as catalysts for olefin metathesis-type reactions presumably due to reduced electrophilicity of the carbene.[12] On the basis of the observations made it is assumed that bisphosphine dinitrosyl alkylidene complexes of rhenium are generally not suitable systems to promote olefin metathesis-type reactions.

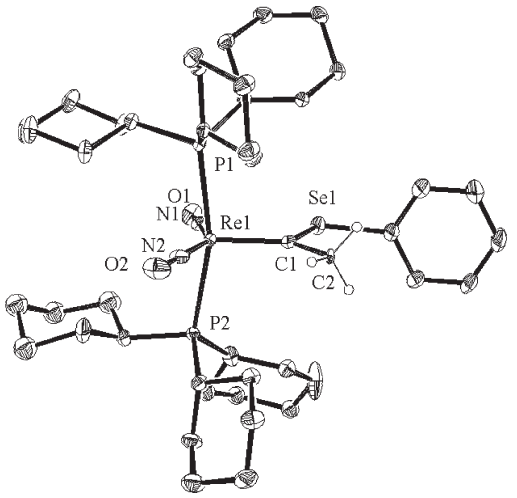


Figure 5. Molecular structure of **7a** with 20% probability displacement ellipsoids. The $[BAr^F_4]^-$ counteranion and all H atoms, with the exception of those from the methyl group, have been omitted for clarity. Selected bond distances (Å) and angles (deg): Re1−N1 = 1.814(5), Re1−N2 = 1.842(5), Re1−C1 = 1.994(5), C1−C2 = 1.535(6), C1−Se1 = 1.875(6), N1−Re1−N2 = 146.73(19), N1−Re1−C1 = 99.5(2), N2−Re1−C1 = 113.8(2), P1−Re1−P2 = 163.63(4).

Experimental Section

General Procedures. All synthetic operations were conducted in oven-dried glassware using a combination of glovebox (M. Braun 150B-G-II), high-vacuum, and Schlenk techniques under dinitrogen atmosphere. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze−thaw cycles prior to use. C_6D_6, C_6D_5Cl, THF-d_8, and methylenechloride-d_2 were purchased from Armar, stored in a Schlenk tube (Teflon tap) over sodium and P_4O_{10}, distilled, and degassed prior to use. All the chemicals were purchased from Aldrich Chemical Co. or Fluka. All reagents were used without

(22) Frech, C. M.; Blacque, O.; Schmalle, H. W.; Berke, H. *Dalton Trans.* **2006**, 4590.

(23) Since the tungsten and molybdenum catalyst precursors $[M(Cl)_2(NO)_2(PR_3)_2]$ (M = Mo and W) show metathesis activity when treated with 2 equiv of $AlCl_2Et$, the catalytically active species of the rhenium system cannot be of the same nature. Moreover, we could show that carbene complexes composed of the cationic dinitrosyl bisphosphine fragment are not active in the olefin metathesis. It is therefore questionable whether the $[M(NO)_2(PR_3)_2]$ (M = Mo and W) frameworks remains intact in the catalytically active species of tungsten and molybdenum catalysts.

(24) *Stoe IPDS software for data collection, cell refinement, and data reduction. Version 2.92*; Stoe & Cie GmbH: Darmstadt, Germany, 1999.

further purification. Preparation of **1a** and **1b** was performed according to the literature.[26]

Physical Measurements. Elemental analyses were performed on a Leco CHNS-932 analyzer at the University of Zurich, Switzerland. ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR data were recorded on a Bruker Avance DRX500 or on a Varian Gemini 300 spectrometer. Chemical shifts are expressed in parts per million (ppm) referenced to the deuterated solvent used. All chemical shifts for ^{31}P{^{1}H} NMR data are reported downfield in ppm relative to external 85% H_3PO_4 at 0.0 ppm. Signal patterns are reported as follows: s, singlet; t, triplet; m, multiplet. IR spectra were obtained by using KBr pellets or ATR methods with a Bio-Rad FTS-45 FTIR spectrometer.

Preparation of [Re(C≡CH)(NHOCH=CH)(NO)(PR$_3$)$_2$][BAr$^F_4$] (R = Cy 3a, R = *i*Pr 3b). Benzene solutions (5 mL) of **1a** (50 mg, 0.030 mmol) or **1b** (50 mg, 0.035 mmol) were set under an acetylene atmosphere and stirred at room temperature. After several minutes a black oily precipitate began to form. After 1 h, the volatiles were removed under reduced pressure and the residue was washed with diethyl ether (2 × 10 mL) and dried under reduced pressure. The pure compound was obtained as a black solid. Yield: 35.4 mg (0.021 mmol; 52%) for **3a** and 33.7 mg (0.023 mmol; 45%) for **3b**. Data for **3a**: Found: C, 54.98; H, 8.34; N, 3.33. Calcd for $C_{38}H_{67}N_2O_2P_2Re$: C, 54.85; H, 8.12; N, 3.37. IR (ATR; cm^{-1}): ν 1601 (m, HNO), 1725 (m, NO), 2090 (w, C≡C). ^{1}H NMR (500 MHz; THF-d_8): 8.72 (br s, 1 H, N*H*OCH=CH), 5.76 (1 H, dt, J_{HH} = 7.6 Hz, J_{PH} = 2.1 Hz, NHOC*H*=CH), 5.02 (1 H, dt, J_{HH} = 7.6 Hz, J_{PH} = 5.8 Hz, NHOCH=C*H*), 4.34 (1 H, unresolved t, J_{PH} = 3.6 Hz, ReC≡C*H*), 2.48−1.03 (66 H, m, P(C$_6$H$_{11}$)$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; THF-d_8): 36.51 (s, *P*(C$_6$H$_{11}$)$_3$). Data for **3b**: Found: C, 40.77; H, 7.51; N, 4.61. Calcd for $C_{20}H_{43}N_2O_2P_2Re$: C, 40.60; H, 7.32; N, 4.73. IR (ATR; cm^{-1}): ν 1600 (m, HNO), 1718 (m, NO), 2091 (w, C≡C). ^{1}H NMR (500 MHz; THF-d_8): 8.90 (br s, 1 H, N*H*OCH=CH), 5.69 (1 H, dt, J_{HH} = 7.7 Hz, J_{PH} = 2.2 Hz, NHOC*H*=CH), 5.26 (1 H, dt, J_{HH} = 7.8 Hz, J_{PH} = 5.9 Hz, 1 H, NHOCH=C*H*) 4.41 (1 H, t, J_{PH} = 3.7 Hz, ReC≡C*H*), 2.56 (6 H, m, P{C*H*(CH$_3$)$_2$}$_3$), 1.37 (m, 36H, P{CH(C*H*$_3$)$_2$}$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; THF-d_8): 43.02 (s, *P*{CH(CH$_3$)$_2$}$_3$).

Preparation of [Re(C≡CH)(NO)$_2$(PR$_3$)$_2$] (R = Cy 4a, R = *i*Pr 4b). To a benzene solution (5 mL) of **1a** (50 mg, 0.030 mmol) or **1b** (50 mg, 0.035 mmol) were added successively an equimolar amount of 2,6-bis(di-*t*Bu)pyridine and an excess of acetylene at room temperature. The dark red solution turned brown immediately. The volatiles were removed under reduced pressure, and the residue was extracted with benzene (2 × 10 mL), filtrated over a cotton pad, followed by the evaporation of the solvent under reduced pressure. The pure compound was obtained as an orange solid. Yield: 23.6 mg (0.029 mmol; 83%) for **4a** and 16.8 mg (0.028 mmol; 80%) for **4b**. Data for **4a**: Found: C, 54.98; H, 8.34; N, 3.33. Calcd for $C_{38}H_{67}N_2O_2P_2Re$: C, 54.85; H, 8.12; N, 3.37. IR (ATR; cm^{-1}): ν 1581 s, NO), 1621 (s, NO). ^{1}H NMR (500 MHz; C$_6$H$_6$): 4.14 (1 H, br s, J_{PH} = 3.9 Hz, ReC≡C*H*), 2.42−1.25 (66 H, m, P(C$_6$H$_{11}$)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz; C$_6$D$_6$): 127.78 (t, J_{PC} = 2.1 Hz, ReC≡*C*H), 111.89 (t, J_{PC} = 19.2 Hz, Re*C*≡CH), 36.39 (vt, J_{PC} = 12.5 Hz, P(*C*$_6$H$_{11}$)$_3$), 30.34 (s, P(C$_6$H$_{11}$)$_3$), 28.26(vt, J_{PC} = 5.4 Hz, P(*C*$_6$H$_{11}$)$_3$), 27.02 (s, P(C$_6$H$_{11}$)$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; C$_6$H$_6$): 20.62 (s, *P*(C$_6$H$_{11}$)$_3$). Data for **4b**: Found: C, 40.77; H, 7.51; N, 4.61. Calcd for $C_{20}H_{43}N_2O_2P_2Re$: C, 40.60; H, 7.32; N, 4.73. IR (ATR; cm^{-1}): ν 1576 (s, NO), 1618 (s, NO). ^{1}H NMR (500 MHz; C$_6$H$_6$): 4.04 (1 H, t, J_{PH} = 4.2 Hz, ReC≡C*H*), 2.43 (6 H, m, P{C*H*(CH$_3$)$_2$}$_3$), 1.33 (m, 36H, P{CH(C*H*$_3$)$_2$}$_3$). ^{13}C{^{1}H} NMR (125.8 MHz; C$_6$D$_6$): 126.32 (t, J_{PC} = 2.2 Hz, ReC≡*C*H), 111.71 (t, J_{PC} = 18.9 Hz, Re*C*≡CH), 26.26 (vt, J_{PC} = 12.8 Hz, P{*C*H(CH$_3$)$_2$}$_3$), 19.84 (s, P{CH(*C*H$_3$)$_2$}$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; C$_6$H$_6$): 26.46 (s, *P*{CH(CH$_3$)$_2$}$_3$).

Preparation of [Re(C=CH$_2$)(NO)$_2$(PR$_3$)$_2$][BAr$^F_4$] (R = Cy 5a, R = *i*Pr 5b). To a methylene chloride solution (10 mL) of **4a** (20 mg, 0.025 mmol) or **4b** (20 mg, 0.030 mmol) was added an equimolar amount of [H(Et$_2$O)][BAr$^F_4$] at room temperature. The yellow solution turned green with stirring for 5 min. The volatiles were removed under reduced pressure, and the residue was washed with pentane (2 × 10 mL) and dried under reduced pressure. The pure compound was obtained as an olive green solid. Yield: 41.2 mg (0.024 mmol; 97%) for **5a** and 41.5 mg (0.029 mmol; 95%) for **5b**. Data for **5a**: Found: C, 49.86; H, 5.01; N, 1.34. Calcd for $C_{70}H_{80}BF_{24}N_2O_2P_2Re$: C, 49.56; H, 4.75; N, 1.65. IR (ATR; cm^{-1}): ν 1751 (m, NO), 1652 (s, NO), 1612 (m, C=C). ^{1}H NMR (500 MHz; CD$_2$Cl$_2$): 7.72 (8 H, m, BAr$^F_4$), 7.49 (4 H, m, BAr$^F_4$), 5.82 (2 H, unresolved triplet, J_{PH} = 2.3 Hz, Re(=CC*H*$_2$)), 2.24−1.19 (36 H, m, P(C$_6$*H*$_{11}$)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz; CD$_2$Cl$_2$): 322.52 (unresolved triplet, Re*C*=CH$_2$)), 162.23 (q, J_{BC} = 49.9 Hz; ipso-B(Ar$^F_4$)$_4$), 135.31 (m; o-B(Ar$^F_4$)$_4$), 128.98 (qq, J_{FC} = 29.5, J_{BC} = 2.9 Hz; m-B(Ar$^F_4$)$_4$), 125.07 (q, J_{FC} = 272.4 Hz ; *C*F$_3$), 122.02 (s, ReC=*C*H$_2$)), 117.86 (septet, J_{FC} = 4.1 Hz; p-B(Ar$^F_4$)), 36.15 (vt, J_{PC} = 10.8 Hz, P(*C*$_6$H$_{11}$)$_3$), 30.31, 27.63, 26.41 (s, P(*C*$_6$H$_{11}$)$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; CD$_2$Cl$_2$): 24.81 (s, *P*(C$_6$H$_{11}$)$_3$). Data for **5b**: Found: C, 43.25; H, 4.13; N, 1.71. Calcd for $C_{52}H_{56}BF_{24}N_2O_2P_2Re$: C, 42.90; H, 3.88; N, 1.92. IR (ATR; cm^{-1}): ν 1753 (s, NO), 1650 (s, NO), 1609 (m, C=C). ^{1}H NMR (500 MHz; CD$_2$Cl$_2$): 7.69 (8 H, m, BAr$^F_4$), 7.51 (4 H, m, BAr$^F_4$), 5.57 (2 H, t, J_{PH} = 2.8 Hz, Re(=CC*H*$_2$)), 2.47 (6 H, m, P{C*H*(CH$_3$)$_2$}$_3$), 1.29 (36 H, m, P{CH(C*H*$_3$)$_2$}$_3$). ^{13}C{^{1}H} NMR (125.8 MHz; CD$_2$Cl$_2$): 320.87 (t, J_{PC} = 15.4 Hz, Re-*C*=CH$_2$)), 162.19 (q, J_{BC} = 49.9 Hz; ipso-B(Ar$^F_4$)), 135.32 (m; o-B(Ar$^F_4$)), 129.00 (qq, J_{FC} = 29.4, J_{BC} = 2.8 Hz; m-B(Ar$^F_4$)), 125.12 (q, J_{FC} = 272.2 Hz, *C*F$_3$), 121.33 (s, ReC=*C*H$_2$)), 117.86 (septet, J_{FC} = 4.0 Hz; p-B(Ar$^F_4$)), 26.76 (vt, J_{PC} = 11.2 Hz, P{*C*H(CH$_3$)$_2$}$_3$), 19.48, 19.11 (s, P{CH(*C*H$_3$)$_2$}$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; CD$_2$Cl$_2$): 31.92 (s, *P*{CH(CH$_3$)$_2$}$_3$).

Preparation of [Re{C(CH$_3$)[S(C$_6$H$_5$)]}(NO)$_2$(PR$_3$)$_2$][BAr$^F_4$] (R = Cy 6a, R = *i*Pr 6b). To a methylene chloride solution (20 mL) of **5a** (50 mg, 0.029 mmol) or **5b** (50 mg, 0.034 mmol) was added a slight excess (1.2 equiv) of thiophenol at room temperature. The green solution turned dark violet while stirring for 10 min. The volatiles were removed under reduced pressure, and the residue was washed with pentane (3 × 10 mL) followed by drying under reduced pressure. The pure compound was obtained as a dark violet solid. Yield: 50.4 mg (0.028 mmol; 94%) for **6a** and 51.1 mg (0.033 mmol; 95%) for **6b**. Data for **6a**: Found: C, 50.62; H, 4.84; N, 1.23. Calcd for $C_{76}H_{86}BF_{24}N_2O_2P_2ReS$: C, 50.49; H, 4.80; N, 1.55. IR (ATR; cm^{-1}): ν 1680 (m, NO), 1631 (s, NO). ^{1}H NMR (500 MHz; CD$_2$Cl$_2$): 7.73 (8 H, m, BAr$^F_4$), 7.58 (3 H, m, ReC(CH$_3$)S(C$_6$*H*$_5$)), 7.52 (4 H, m, BAr$^F_4$), 7.33 (2 H, m, ReC(CH$_3$)(C$_6$*H*$_5$)), 3.23 (3 H, s, ReC(C*H*$_3$)S(C$_6$H$_5$)), 2.20−1.23 (66 H, m, P(C$_6$*H*$_{11}$)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz; CD$_2$Cl$_2$): 300.53 (unresolved triplet, Re*C*(CH$_3$)S(C$_6$H$_5$)), 162.09 (q, J_{BC} = 49.8 Hz; ipso-B(Ar$^F_4$)$_4$), 148.16 (s, ReC(CH$_3$)-S(*C*$_6$H$_5$)), 135.27 (m, o-B(Ar$^F_4$)$_4$), 133.62, 132.54, 131.90, 131.00 (s, ReC(CH$_3$)S(*C*$_6$H$_5$)), 128.98 (qq, J_{FC} = 29.4, J_{BC} = 2.8 Hz; m-B(Ar$^F_4$)$_4$), 125.11 (q, J_{FC} = 272.4 Hz ; *C*F$_3$), 117.83 (septet, J_{FC} = 4.0 Hz; p-B(Ar$^F_4$)), 123.05 (s, ReC(CH$_3$)S(*C*$_6$H$_5$)), 45.76 (s, ReC(*C*H$_3$)S(C$_6$H$_5$)), 36.10 (vt, J_{PC} = 11.4 Hz, P(*C*$_6$H$_{11}$)$_3$), 29.66, 29.34, 28.82, 27.32, 26.02 (s, P(C$_6$H$_{11}$)$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; CD$_2$Cl$_2$): 9.98 (s, *P*(C$_6$H$_{11}$)$_3$). Data for **6b**: Found: C, 44.37; H, 4.16; N, 1.72. Calcd for $C_{58}H_{62}BF_{24}N_2O_2P_2ReS$: C, 44.45; H, 3.99; N, 1.79. IR (ATR; cm^{-1}): ν 1685 (m, NO), 1634 (s, NO). ^{1}H NMR (500 MHz; CD$_2$Cl$_2$): 7.71 (8 H, m, BAr$^F_4$), 7.57 (3 H, m, Re=C(CH$_3$)S(C$_6$*H*$_5$)), 7.54 (4 H, m, BAr$^F_4$), 7.33 (2 H, m, ReC(CH$_3$)S(C$_6$*H*$_5$)), 3.33 (3 H, s, Re=C(C*H*$_3$)S(C$_6$H$_5$)), 2.57 (6 H, m, P{C*H*(CH$_3$)$_2$}$_3$), 1.29 (36 H, m, P{CH(C*H*$_3$)$_2$}$_3$). ^{13}C{^{1}H} NMR (125.8 MHz; CD$_2$Cl$_2$): 304.65 (t, J_{PC} = 3.5 Hz, Re*C*(CH$_3$)S(C$_6$H$_5$)), 162.08 (q, J_{BC} = 49.9 Hz; ipso-B(Ar$^F_4$)$_4$), 148.47 (s, ReC(CH$_3$)S(*C*$_6$H$_5$)), 135.22 (m, *o*-B(Ar$^F_4$)$_4$), 133.17, 132.50, 132.13, 131.00 (s, ReC(CH$_3$)S(*C*$_6$H$_5$)), 129.11 (qq, J_{FC} = 29.5, J_{BC} = 2.8 Hz; m-B(Ar$^F_4$)$_4$), 125.06

(25) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.
(26) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, 112.

Table 1. Crystallographic Data of 4b, 5b, and 7a

parameter	4b	5b	7a
chemical formula	$C_{20}H_{43}N_2O_2P_2Re$	$C_{52.125}H_{56.25}BCl_{0.25}F_{24}N_2O_2P_2Re$	$C_{167}H_{208}B_2F_{48}N_4O_4P_4Re_2Se_2$
fw [g mol^{-1}]	591.71	1466.56	3923.21
cryst habit, color	plate, red	block, green	plate, violet
cryst dimens [mm]	0.35 × 0.30 × 0.10	0.33 × 0.29 × 0.22	0.26 × 0.19 × 0.07
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.8793(8)	12.3890(7)	14.4760(14)
b [Å]	13.7535(9)	19.2742(11)	17.1882(16)
c [Å]	15.6869(11)	26.7543(15)	20.163(2)
α [deg]	90	76.765(6)	70.232(11)
β [deg]	95.817(8)	85.778(7)	74.210(11)
γ [deg]	90	89.584(7)	83.273(11)
V [Å^3]	2549.8(3)	6201.7(6)	4541.3(9)
Z	4	4	1
T [K]	123(2)	183(2)	183(2)
D_{calcd} [gcm^{-3}]	1.541	1.571	1.434
μ [mm^{-1}]	4.907	2.133	1.867
R1[a], wR2[b] ($I > 2\sigma(I)$)	0.0264, 0.663	0.0509, 0.1278	0.0442, 0.1016
R1[a], wR2[b] (all data)	0.0396, 0.0683	0.0710, 0.1355	0.0733, 0.1076

[a] $R(F) = \sum||F_o|-|F_c||\sum|F_o|$. [b] $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$.

(q, J_{FC} = 272.5 Hz, CF_3), 117.92 (septet, J_{FC} = 4.0 Hz; p-B(Ar^F_4)), 46.23 (s, ReC(CH_3)S(C_6H_5)), 26.59 (vt, J_{PC} = 14.5 Hz, P{CH-(CH_3)$_2$}$_3$), 19.54, 19.14 (s, P{CH(CH_3)$_2$}$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz; CD_2Cl_2): 20.00 (s, P{CH(CH_3)$_2$}$_3$).

Preparation of [Re{C(CH_3)[Se(C_6H_5)]}(NO)$_2$(PR_3)$_2$][BAr^F_4] (R = Cy 7a, R = *i*Pr 7b). To a methylene chloride solution (20 mL) of **5a** (50 mg, 0.029 mmol) or **5b** (50 mg, 0.034 mmol) was added a slight excess (1.2 equiv) of benzoselenol at room temperature. The green solution turned dark violet while stirring for 10 min. The volatiles were removed under reduced pressure, and the residue was washed with pentane (3 × 10 mL) followed by drying under reduced pressure. The pure compound was obtained as a dark violet solid. Yield: 51.4 mg (0.028 mmol; 94%) for **5a** and 52.4 mg (0.033 mmol; 95%) for **7b**. Data for **7a**: Found: C, 49.50; H, 4.39; N, 1.35. Calcd for $C_{76}H_{86}BF_{24}N_2O_2P_2ReSe$: C, 49.25; H, 4.68; N, 1.51. IR (ATR; cm^{-1}): ν 1696 (m, NO), 1635 (s, NO). ^1H NMR (500 MHz; CD_2Cl_2): 7.72 (8 H, m, BAr^F_4), 7.57 (3 H, m, ReC(CH_3)Se(C_6H_5)), 7.54 (4 H, m, BAr^F_4), 7.45 (2 H, m, ReC-(CH_3)Se(C_6H_5)), 3.38 (3 H, s, ReC(CH_3)Se(C_6H_5)), 2.14−1.23 (66 H, m, P(C_6H_{11})$_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz; CD_2Cl_2): 300.63 (unresolved triplet, ReC(CH_3)Se(C_6H_5)), 162.16 (q, J_{BC} = 49.9 Hz; ipso-B(Ar^F_4)$_4$), 148.47 (s, ReC(CH_3)Se(C_6H_5)), 135.25 (m, o-B(Ar^F_4)$_4$), 133.50, 131.01, 130.86, (s, ReC(CH_3)Se-(C_6H_5)), 129.14 (qq, J_{FC} = 29.4, J_{BC} = 2.9 Hz; *m*-B(Ar^F_4)$_4$), 125.16 (q, J_{FC} = 272.4 Hz, CF_3), 117.95 (septet, J_{FC} = 4.1 Hz; p-B(Ar^F_4)), 48.56 (s, ReC(CH_3)Se(C_6H_5)), 36.19 (vt, J_{PC} = 11.4 Hz, P(C_6H_{11})$_3$), 29.68, 29.27, 28.84, 27.26, 26.02 (s, P(C_6H_{11})$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz; CD_2Cl_2): 7.33 (s, P(C_6H_{11})$_3$). Data for **7b**: Found: C, 44.37; H, 4.16; N, 1.72. Calcd for $C_{58}H_{62}BF_{24}N_2O_2P_2ReSe$: C, 43.19; H, 3.87; N, 1.74. IR (ATR; cm^{-1}): ν 1685 (m, NO), 1634 (s, NO). ^1H NMR (500 MHz; CD_2Cl_2): 7.71 (8 H, m, BAr^F_4), 7.57 (3 H, m, Re=C(CH_3)Se-(C_6H_5)), 7.54 (4 H, m, BAr^F_4), 7.33 (2 H, m, ReC(CH_3)Se(C_6H_5)), 3.33 (3 H, s, Re=C(CH_3)Se(C_6H_5)), 2.51 (6 H, m, P{CH(CH_3)$_2$}$_3$), 1.25 (36 H, m, P{CH(CH_3)$_2$}$_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz; CD_2Cl_2): 306.32 (t, J_{PC} = 3.5 Hz, ReC(CH_3)Se(C_6H_5)), 162.14 (q, J_{BC} = 49.9 Hz; ipso-B(Ar^F_4)$_4$), 148.47 (s, ReC(CH_3)Se(C_6H_5)), 135.25 (m, o-B(Ar^F_4)$_4$), 132.35, 131.29, 130.96 (s, ReCHSe-(C_6H_5)), 129.18 (qq, J_{FC} = 29.5, J_{BC} = 2.9 Hz; m-B(Ar^F_4)$_4$), 125.23 (q, J_{FC} = 272.5 Hz, CF_3), 117.98 (septet, J_{FC} = 4.2 Hz; p-B(Ar^F_4)), 49.06 (s, ReC(CH_3)Se(C_6H_5)), 26.76 (vt, J_{PC} = 14.5 Hz, P{CH(CH_3)$_2$}$_3$), 19.50, 19.10 (s, P{CH(CH_3)$_2$}$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz; CD_2Cl_2): 17.85 (s, P{CH(CH_3)$_2$}$_3$).

X-ray Diffraction Analysis of 4b, 5b, and 7a. X-ray diffraction studies were performed on a Stoe IPDS diffractometer, where it was cooled to 123(2) K for **4b** and to 183(2) K for **5b** and **7a**. Crystals of **4b**, **5b**, and **7a** protected in hydrocarbon oil were selected using a polarizing microscope. The crystals were mounted on a tip of a glass fiber and immediately transferred to the goniometer of an imaging plate detector system (Stoe IPDS diffractometer) and cooled to 183(2) K using an Oxford Cryogenic System. The crystal-to-image distance was set to 50 mm (θ_{max} = 30.245°) for **4b**, 70 mm (θ_{max} = 25.90°) for **5b**, and 60 mm (θ_{max} = 27.95°) for **7a**. The φ-oscillation scan modes were applied for the intensity measurement. For the cell parameter refinement for **4b**, **5b**, and **7a**, 7997, 7996, and 8000 reflections were selected out of the whole limiting sphere. A total of 29 609, 54 386, and 72 540 diffraction intensities were collected,[24] of which 7371, 22 563, and 20 147 were independent (R_{int} = 0.0471, 0.0536, and 0.0681) after data reduction. Numerical absorption correction[25] based on 15, 16, and 9 crystal faces was applied with the FACEitVIDEO and XRED programs.[24] The structure was solved by the Patterson method using the SHELXS97 program package.[26] Interpretation of the difference Fourier maps, preliminary plot generations, and checking for higher symmetry were performed with the PLATON program[27] and the implemented in the LEPAGE program.[28] All heavy atoms were refined (SHELXL97)[26] using anisotropic displacement parameters. Positions of H atoms were calculated after each refinement cycle (riding model). The structural plots were generated using the ORTEP program.[29]

Acknowledgment. This work was funded by the Swiss National Science Foundation (SNSF) and the University of Zurich.

Supporting Information Available: CIF files containing X-ray crystallographic data for complexes **4b** (CCDC-606740), **5b** (CCDC-606741), and **7a** (CCDC-606742) and energies and Cartesian coordinates of all calculated intermediates and transition states. This material is available free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, at http://pubs.acs.org, or from the author.

(27) (a) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7. (b) Spek, A. L. *Acta Crystallogr. Sect. D* **2009**, 148.
(28) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264.
(29) Johnson C. K. *ORTEPII. Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.