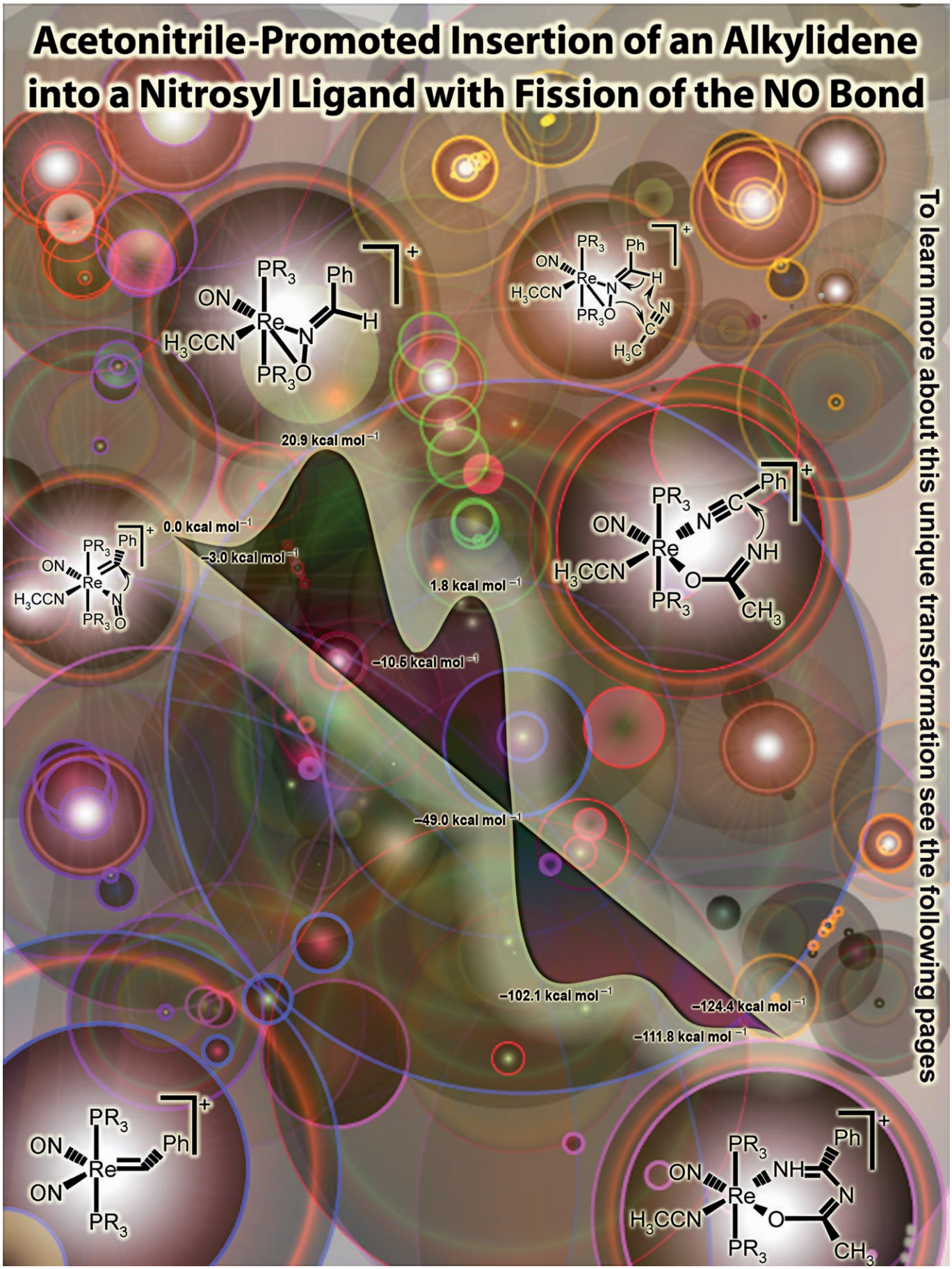


CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600286

Metal Nitrosyl Reactivity: Acetonitrile-Promoted Insertion of an Alkylidene into a Nitrosyl Ligand with Fission of the NO Bond

C. M. Frech, O. Blacque, H. W. Schmalle, and H. Berke*[a]

Abstract: Treatment of the complexes $[Re(NO)_2(PR_3)_2][BAr^F_4]$ (R = Cy, **1a**; R = *i*Pr, **1b**) with phenyldiazomethane gave the cationic benzylidene species $[Re\{CH(C_6H_5)\}(NO)_2(PR_3)_2][BAr^F_4]$ (**2a** and **2b**) in good yields. Upon reaction of **2a** and **2b** with acetonitrile, the consecutive formation of $[Re(N{\equiv}CCH_3)(N{\equiv}CPh)(NO)(OC(CH_3){=}NH)(PR_3)][BAr^F_4]$ (**3a** and **3b**) and $[Re(NCCH_3)(OC\{CH_3\}NH\{C_6H_5\})(NO)(PR_3)_2][BAr^F_4]$ (**4a** and **4b**) was observed. The proposed reaction sequence involves the coupling of coordinated NO, carbene and acetonitrile molecules to yield the (1*Z*)-*N*-[imino(phenyl)methyl]ethanimidate ligand. The coupling of the nitrosyl and the benzylidene is anticipated to occur first, forming an oximate species. The subsequent acetonitrile addition can be envisaged as a heteroene reaction of the oximate and the acetonitrile ligand yielding **3a** and **3b**, which in turn can cyclise and undergo a prototropic shift initiated by an internal attack of the ethaneimidate ligand on the benzonitrile moiety to afford **4a** and **4b**.

Keywords: alkylidene · N–C bond formation · NO insertion · reaction mechanisms · rhenium

Introduction

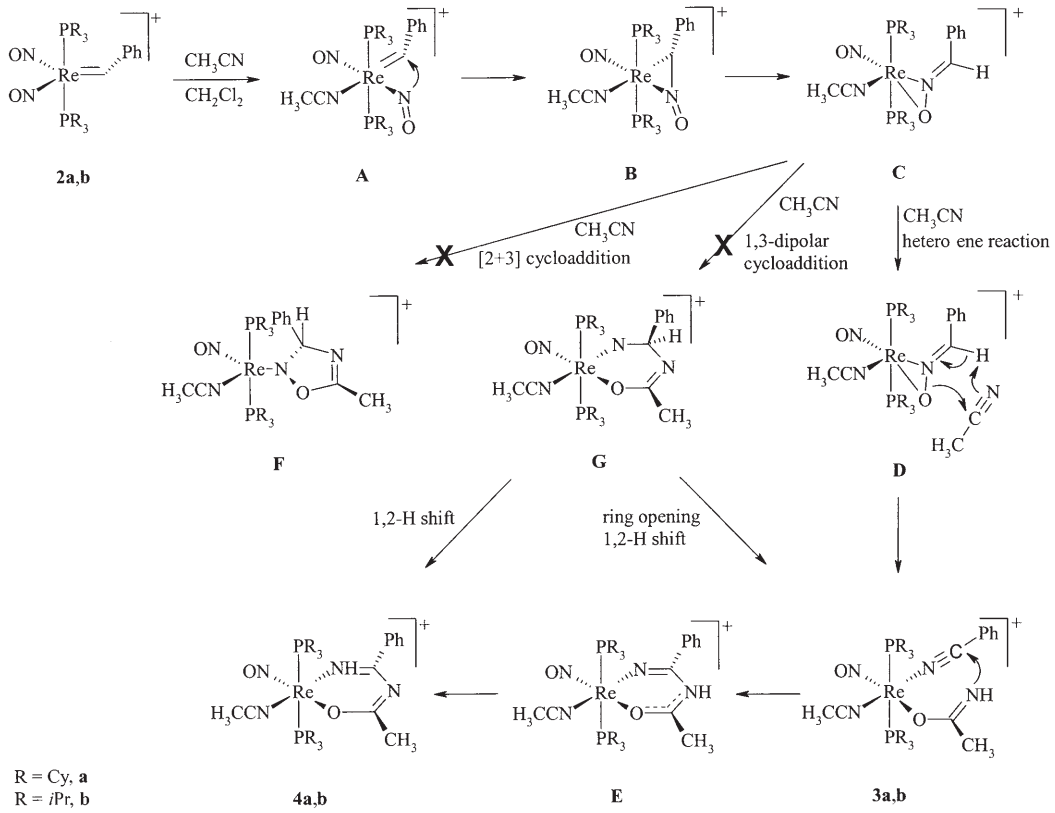
Reactions on coordinated π-acceptor ligands belong to an important class of organometallic transformations,[1] because they often provide facile access to molecular arrangements that are sometimes difficult or even impossible to obtain by conventional organic routes.[2,3] Comparable to the CO-insertion reaction, the selective formation of C–N bonds from NO insertion would be desirable for production of both fine and commodity chemicals.[1g,4–6] In contrast to the ubiquitous CO insertion, the related shift of alkyl units onto NO is confined to only a few reported examples. The first direct observation of the conversion of a well-defined alkyl–nitrosyl complex into a *C*-nitroso–alkane species was reported by H. Klein et al. in 1976.[7] Other examples were published subsequently by the group of R. G. Bergman.[3] Related couplings of carbene with π-acceptor ligands are rare, although the metal-mediated coupling of an alkylidene and CO to produce a ketene moiety is known.[8] The related conversions of alkylidene units with coordinated nitrosyl ligands are yet unknown chemical transformations, but were found to exist as a unique step in the reaction sequence of $[Re(=CHPh)(NO)_2(PR_3)_2][BAr^F_4]$ complexes (**2a** and **2b**) induced by acetonitrile.[9] The reactions of such benzylidene complexes with acetonitrile were first thought to be related to studies of R. Beckhaus reporting the [2+2] addition reaction of the titanium vinylidene complex $[Cp^*_2Ti(=CCH_2)]$ with organonitrile compounds.[10] However, the reactions of **2a** and **2b** with acetonitrile turned out to be much more complicated, showing a sequence of elementary steps involving the coupling of the benzylidene and the NO ligand. Detailed investigations of the reaction course, including labelling studies and theoretical modelling, led us to propose a plausible reaction mechanism.

[a] Dr. C. M. Frech, Dr. O. Blacque, Dr. H. W. Schmalle, Prof. Dr. H. Berke
Department of Inorganic Chemistry, University of Zürich
8057 Zürich (Switzerland)
Fax: (+41) 44-635-6802
E-mail: hberke@aci.unizh.ch

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Cartesian coordinates and computed total bonding energies of optimised geometries.

Results and Discussion

The treatment of benzene solutions of the cationic complexes $[Re(NO)_2(PR_3)_2][BAr^F_4]$ (R = Cy, **1a**; R = *i*Pr, **1b**) with phenyldiazomethane at room temperature gave the moderately stable benzylidene complexes $[Re(=CHPh)(NO)_2(PR_3)_2][BAr^F_4]$ (**2a** and **2b**) in good yields (Scheme 1).[9] As a large stoichiometric excess of acetonitrile was added to CH_2Cl_2 solutions of the benzylidene complexes **2a** and **2b** at −30 °C, exclusive formations of $[Re(N{\equiv}CCH_3)(N{\equiv}CPh)(NO)(OC(CH_3){=}NH)(PR_3)][BAr^F_4]$ (**3a** and **3b**)



Scheme 1.

were observed. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed new singlet resonances at $\delta = -2.8$ and 6.12 ppm assigned to the products **3a** and **3b**. Signals due to intermediates could not be observed. Complete conversion was achieved overnight, accompanied by a colour change from dark-red to orange. Compounds **3a** and **3b** were isolated in almost quantitative yields. The ^1H NMR spectra of **3a** and **3b** displayed, in addition to the phosphine signals, singlets at $\delta = 2.94$ and 2.90 ppm. These correlated to $^{13}C\{^1H\}$ NMR signals in the two-dimensional spectra at $\delta =$ 139.0 and 138.9 ppm and at $\delta = 5.3$ and 5.1 ppm, respectively. These resonances are, thus, consistent with the coordination of one acetonitrile to the metal centre. Additional singlets were detected in the ^1H NMR spectra at $\delta = 1.92$ and 4.14 ppm (**3a**) as well as at $\delta = 1.85$ and 4.15 ppm (**3b**). In the two-dimensional spectra these signals correlated with the $^{13}C\{^1H\}$ NMR signals at $\delta = 177.4$ and 177.8 ppm, respectively. The ^1H NMR signals at $\delta = 1.92$ and 1.85 ppm were assigned to methyl groups, whereas those at $\delta = 4.14$ and 4.15 ppm have a typical chemical shift for imine protons, implying the generation of an ethanimidate ligand. The formation of this moiety was confirmed for both cases by reactions using ^{15}N-labelled acetonitrile. The $^{15}N\{^1H\}$ NMR spectra of **3a** and **3b** show two strong signals at $\delta = -213.4$ and -250.0 ppm and at $\delta = -215.0$ and -250.3 ppm, respectively, of which the signals at $\delta = -213.4$ and -215.0 ppm were assigned to the coordinated acetonitrile molecule. The resonances at $\delta = -250.0$ and -250.3 ppm correlate with the nitrogen-bound hydrogen atoms at $\delta = 4.14$ and 1.92 ppm and at $\delta = 4.15$ and 1.85 ppm. Interestingly, no ^1H NMR signals were detected in the region characteristic for alkylidene hydrogen atoms, which indicates transformation of the benzylidene unit. The IR spectra of **3a** and **3b** exhibit two weak bands for both complexes, at 2270 and 2229 cm^{-1} and at 2271 and 2228 cm^{-1}, respectively, attributable to different types of nitrile units. A further intense absorption band at 1704 and 1697 cm^{-1}, respectively, is consistent with the presence of a mononitrosyl complex. Compound **3a** could be confirmed further in its molecular structure by MS, which revealed fragmentations expelling benzonitrile, two subsequent acetonitrile molecules and tricyclohexyl phosphine. The reaction sequence of $[Re(=CHPh)(NO)_2(PR_3)][BAr^F_4]$ (**2a** and **2b**) with acetonitrile leading to **3a** and **3b** is represented in Scheme 1.

Attempts to crystallise any of the $[Re(N{\equiv}CCH_3)(N{\equiv}CPh)(NO)(OC(CH_3){=}NH)(PR_3)][BAr^F_4]$ complexes to obtain X-ray-quality crystals failed, because of impurities caused by the consecutive transformation of these compounds into the cationic phosphine derivatives of $[Re(NCCH_3)(OC\{CH_3\}NH\{C_6H_5\})(NO)(PR_3)_2][BAr^F_4]$ **4a** and **4b**. These subsequent transformations turned out to be solvent independent (tetrahydrofuran, methylene chloride, diethyl ether or acetonitrile), and were complete after two days at room temperature. Compounds **4a** and **4b** were isolated in quantitative yields. Higher reaction temperatures were inappropriate, as they promoted the formation of side

products. The ^{1}H NMR spectra of **4a** and **4b** in CD_2Cl_2 showed, in addition to phenyl and the phosphine protons, broad resonances at $\delta = 8.76$ and 8.78 ppm characteristic for the formed (1*Z*)-*N*-[imino(phenyl)methyl]ethanimidate ligand. In the two-dimensional spectra these resonances correlated with the $^{13}C\{^1H\}$ NMR signals at $\delta = 163.6$ and 164.0 ppm, confirming the presence of the imino(phenyl) moiety. In the ^{1}H NMR spectra of **4a** and **4b** two further sharp singlets appeared at $\delta = 2.89$ and 2.36 ppm and at $\delta =$ 2.94 and 2.38 ppm, respectively. The resonances at $\delta = 2.89$ and 2.94 ppm were assigned to acetonitrile ligands. The signals at $\delta = 2.36$ and 2.38 ppm correlated in two-dimensional NMR spectra with the $^{13}C\{^1H\}$ NMR signals at $\delta = 176.9$ and 29.8 ppm and at $\delta = 177.1$ and 29.6 ppm, consistent with the formation of (1*Z*)-*N*-[imino(phenyl)methyl]ethanimidate ligands. This assignment is further supported by $^{15}N\{^1H\}$ NMR spectroscopy and ^{1}H, $^{15}N\{^1H\}$ correlation experiments of the ^{15}N-labelled complexes **4a** and **4b**. The $^{15}N\{^1H\}$ NMR signals at $\delta = -207.9$ and -209.4 ppm are due to the coordinated acetonitrile ligands. The signals at $\delta = -163.5$ and -163.9 ppm are shifted significantly upfield ($\Delta\delta \approx 90$ ppm) and have no correlation to any proton signal, indicating a reaction sequence with formation of a carbon–nitrogen bond and a concomitant proton shift. The structures of **4a** and **4b** were established by an X-ray diffraction study on crystals of **4b** (Figure 1). Single crystals were obtained by slow evaporation of a concentrated methylene chloride solution at $-30\,^\circ$C. The rhenium centre possesses a pseudooctahedral environment with the nitrosyl and acetonitrile ligands displaced *cis*. The chelating (1*Z*)-*N*-[imino(phenyl)methyl]ethanimidate ligand occupies positions *trans* to these ligands with the presumably more-labile oxygen atom opposite to NO. The C23–N3 and C21–N4 bond lengths of 1.307(4) and 1.321(4) Å, respectively, have rather double-bond character, whereas the N4–C23 and O2–C21 bond lengths of 1.373(4) and 1.294(4) Å, respectively, refer to relatively short single bonds, suggesting a delocalised chelate ligand, similar to the isoelectronic β-diketonates and β-diiminato ligands. The imine hydrogen atom H3 was located in the difference Fourier map and was refined isotropically.

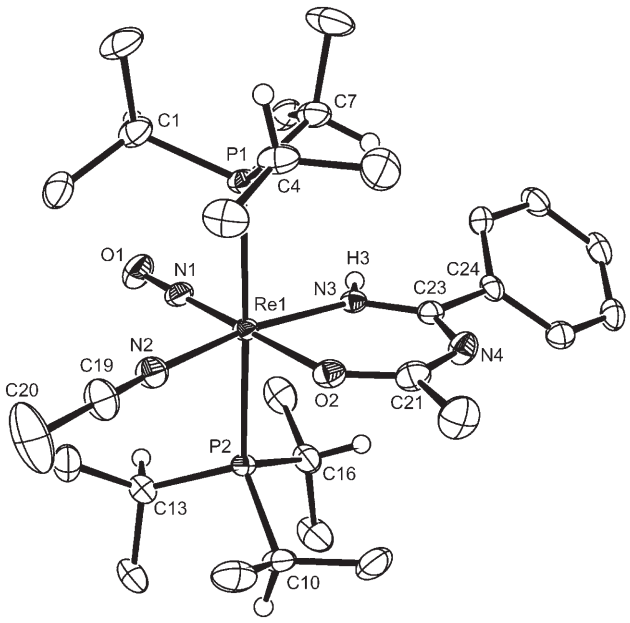


Figure 1. Molecular structure of **4b** (50% probability displacement ellipsoids). The hydrogen atom H3 was refined isotropically. The $[BAr^F_4]^-$ counterion and all hydrogen atoms, with exception of H3 and those of the isopropyl groups, have been omitted for clarity. Selected bond lengths (Å) and angles (°): Re1–N1 1.763(3), Re1–N2 2.088(3), Re1–N3 2.074(3), Re1–O2 2.064(2), O2–C21 1.294(4), C21–N4 1.321(4), N4–C23 1.373(4), C23–N3 1.307(4); N3-Re1-O2 82.70(10).

Unfortunately, it was not possible to detect spectroscopically any intermediates other than **3a** and **3b**. Even the acetonitrile adducts of **2a** and **2b** could not be observed, despite the fact that the DFT calculations indicated their slightly stabilised nature with respect to **1a** and **1b**. As **2a** and **2b** were treated with trimethylphosphine to eventually promote the NO–alkylidene coupling and trap the oximate species, the formation of several phosphorous-containing compounds occurred. Attempts to identify spectroscopically or to separate one of these products from the reaction mixtures failed.

From the reaction of **2a** and **2b** with ^{15}N-labelled acetonitrile conclusive mechanistic insights were obtained. Most importantly, it was shown that the nitrogen atom of the benzonitrile ligand of **3a** and **3b** originates from the NO ligand. Hence, the products formed in this reaction sequence indeed involved the coupling of one of the NO ligands with the benzylidene ligand, with the plausible intermediates **A**, **B** and **C** referring also to a shift of the formed oximate ligand from C, N to N, O binding to rhenium. The formation of the bent NO species **A** gains support from the reaction of a related hydridodinitrosylbis(triphenylphosphine)rhenium complex $[Re(H)(NO)_2(PPh_3)_2]$ with HCl, resulting in the corresponding dichloro–nitroxyl complex $[Re(Cl)_2(NH{=}O)(NO)(PPh_3)_2]$,[11] in which a primary nucleophilic attack of Cl^- is followed by protonation of one of the bent nitrosyl ligands. Another related example is the recently reported reaction of the cationic dinitrosyl complex $[Re(NO)_2(PR_3)_2]^+$ with phenylacetylene, yielding the {1-[(aminooxy)methyl]-vinyl}benzene complexes $[Re(C{\equiv}CPh)(CH{=}C(Ph)ONH)(NO)(PR_3)_2]$, for which R = Cy or *i*Pr. This is among other steps thought to proceed with initial acetylene attack on rhenium and proton transfer to the bent NO.[12]

In a further step, either a 1,3-dipolar cycloaddition, a [2+3] cycloaddition or a pericyclic heteroene-type reaction between the azaketenate ligand in **C** and an acetonitrile molecule could take place. 1,3-Dipolar cycloadditions are known from organic nitrones and nitriles. This would lead to an [(amido)(phenyl)methyl]ethanimidato ligand in intermediate **G**. If a [2+3] cycloaddition occurs, a 5-methyl-3-phenyl-1,2,4-oxadiazol-2(3*H*)-yl complex **F** would be generated, which is analogous to reactions of nitrones with nitriles observed in the ligand sphere of platinum–benzonitrile complexes $[Pt(Cl)_2(N{\equiv}CPh)_2]$.[13] However, transformations giving intermediates **F** or **G** can be ruled out, as these intermediates could hardly be transformed in simple steps into

the identified benzonitrile ethaneimidate complexes **3a** and **3b**. Although intermediate **F** would mark a dead end in the reaction sequence, intermediate **G** could be envisaged to be converted directly into **4a** and **4b** by a simple proton shift. This is not observed, therefore, a pericyclic heteroene-type reaction between the azaketenate ligand in **C** and an acetonitrile molecule (see Scheme 1) is anticipated to be the most plausible route for the transformation of **C** into **3a** and **3b**.[14,15] The conversion of **3a** and **3b** into **4a** and **4b** involves a nucleophilic attack of the imino group onto the $C_{benzonitrile}$ followed by a proton migration.

DFT analysis: To support the mechanism of the transformation of **2a** and **2b** into **3a** and **3b** and the subsequent formation of the (1*Z*)-*N*-[imino(phenyl)methyl]ethanimidate complexes **4a** and **4b**, given in Scheme 1, density functional theory (DFT) calculations were carried out on PMe_3-substituted model derivatives. These began with calculations on the $[Re\{CH(C_6H_5)\}(NO)_2(PMe_3)_2]^+$ complex **2**-Me and revealed that the LUMO of this cationic species is composed mainly of dominating $p_{benzylidene}$ character and the in-phase π* combination of the NO groups (Figure 2). The second

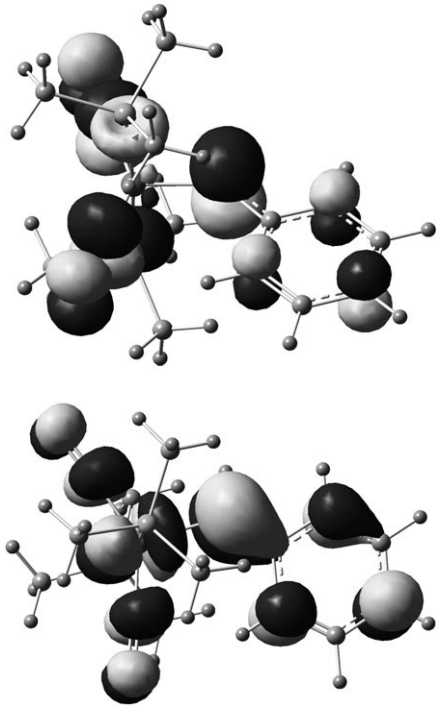


Figure 2. Shapes and phases of the LUMO (top) and the SUMO (bottom) of the cationic model complex $[Re(=CHPh)(NO)_2(PMe_3)_2]^+$ **2**-Me.

unoccupied molecular orbital (0.95 eV higher in energy than the LUMO) is similar in shape to the LUMO with NO π*-orbital contribution, but in contrast to the LUMO, there is a further strong out-of-phase rhenium d-orbital character. These empty frontier orbitals signal the electrophilic character of **2a** and **2b**, which facilitates the nucleophilic attack of any Lewis base. A frontier-orbital-controlled nucleophilic attack of acetonitrile could, therefore, be envisaged to occur either on the Re centre to form the octahedral intermediate **A**-Me or on the $C_{carbene}$ atom leading alternatively to the nitrilium ylid complex **A**′-Me. The alternative attack on a NO π^* orbital would be expected to establish a thermodynamically weak N–N bond. In accord with this, such a reaction step is not precedented by literature reports.

The two isomers **A**-Me and **A**′-Me are relatively close in energy; **A**-Me is favoured over complex **A**′-Me by only $\Delta E_0 = +6.0\ kcal\,mol^{-1}$ (calculated $\Delta\Delta G = +5.2\ kcal\,mol^{-1}$). The computed energy differences ΔE_e (classical electronic energies computed at the *m*PW1PW91 level), ΔE_0 ($\Delta E_0 = \Delta E_e + \Delta(ZPE)$), ΔE_{sol} ($\Delta E_{PCM} + \Delta(ZPE)$, in which ΔE_{PCM} represents the relative electronic energies after PCM solvation correction) and ΔG (relative Gibbs free energy) of all optimised species relative to the energetics of **2**-Me are given in Table 1. The coordination of the acetonitrile to the rhenium

Table 1. Computed relative energies[a] [$kcal\,mol^{-1}$] and lowest harmonic frequencies [cm^{-1}] of the species studied.

Complex	ΔE_e	ΔE_0	ΔE_{sol}	ΔG	ν_{min}
2-Me	0.0	0.0	0.0	0.0	+27.5
A-Me	−3.5	−3.0	−0.2	+9.3	+9.5
A′-Me	+0.8	+3.0	+1.8	+14.5	+14.0
TS1	+20.1	+20.9	+23.7	+32.9	−183.8
B-Me	−13.0	−10.5	−8.5	+1.7	+25.9
TS2	−0.1	+1.8	+3.5	+14.7	−176.2
C-Me	−51.9	−49.0	−46.5	−37.5	+20.5
3-Me	−107.2	−102.1	−95.8	−77.7	+16.8
D-Me	−118.2	−111.8	−107.4	−85.9	+16.4
4-Me	−131.3	−124.4	−118.2	−100.6	+12.6
2-Me	0.0	0.0	0.0	0.0	+27.5
TS1′	+42.8	+42.2	+42.1	+42.0	−307.7
B′-Me	+22.1	+23.2	+22.0	+23.9	+31.8
E-Me	+8.9	+11.7	+16.5	+34.3	+14.4
F-Me	−44.2	−39.1	–	−13.6	+20.4

[a] Definitions of the energetics are: ΔE_e, classical relative electronic energies computed at the *m*PW1PW91 level; $\Delta E_0 = \Delta E_e + \Delta(ZPE)$; $\Delta E_{sol} = \Delta E_{PCM} + \Delta(ZPE)$, for which ΔE_{PCM} is the relative electronic energy after PCM solvation correction; ΔG, relative Gibbs free energy.

centre is energetically slightly downhill ($-3.0\ kcal\,mol^{-1}$) and induces bending of both M-N-O moieties (139.4 and 141.8°) in **A**-Me and, thus, enforces NO to act as a one-electron ligand (Figure 3). The bent nitrosyl ligands were found to be further stabilised by weak hydrogen-bonding interactions with the hydrogen atom of the carbene ligand and with one *ortho*-hydrogen atom of the phenyl ring (N···H = 2.73 and 2.34 Å, respectively). These relatively short N···H contacts witness additional energetic stabilisation of isomer **A**-Me, so that it becomes more stable than **A**′-Me. However, species **A**′-Me appears to be located on a nonproductive pathway, making its existence in equilibrium plausible, but not allowing further transformation.

In **A**-Me, in contrast to **2**-Me, the N_{NO} atoms come closer to the $C_{carbene}$ atom, preparing the complex for carbene/NO coupling (Figure 4).

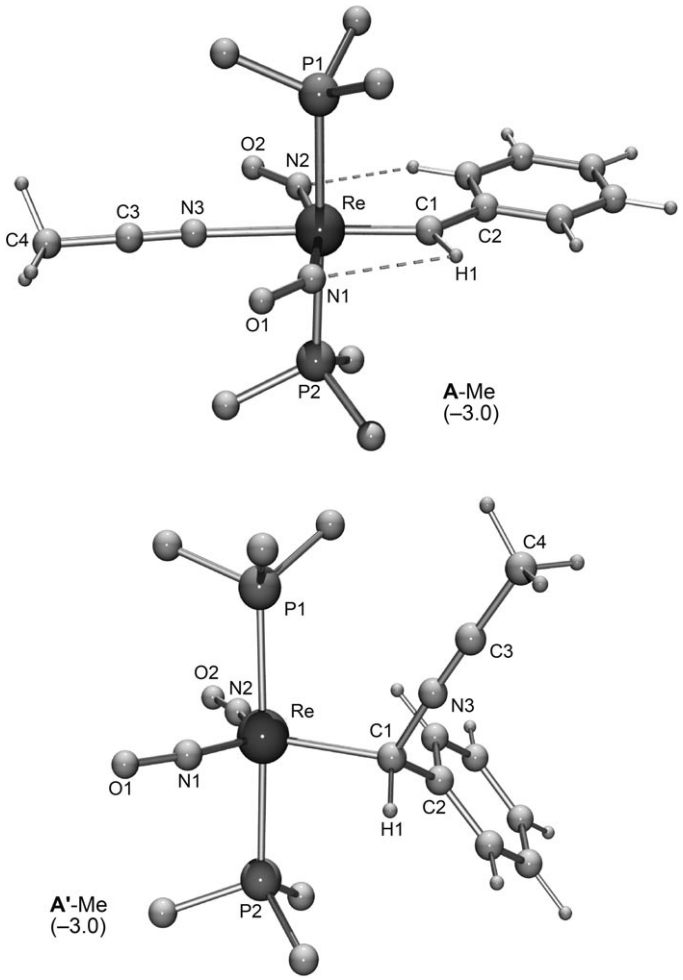


Figure 3. DFT-optimised structures and relative energies of the model complexes **A**-Me and **A**′-Me. Important geometrical parameters are as follows. **A**-Me: Re–C1 = 1.96, N1···C1 = 2.87 Å; Re-N1-O1 = 139.4, Re-N2-O2 = 141.8, N1-Re-C1 = 94.1, N2-Re-C1 = 101.5°. **A**′-Me: Re–C1 = 2.30 Å; N1-Re-C1 = 116.7, N2-Re-C1 = 121.7°.

In the fashion of a migratory insertion, this corresponds to a nucleophilic attack of one of the bent nitrosyl nitrogen atoms on the carbene carbon atom being exothermic by $\Delta\Delta E_0 = -7.5$ kcal mol^{-1}, and leads to the *C*-nitroso complex **B**-Me ($\Delta E_0 = -10.5$ kcal mol^{-1}) with a significant calculated barrier of $\Delta\Delta E_0^{\neq} = +23.9$ kcal mol^{-1} (**TS1**). Thus, **TS1** represents the highest energetic point on the reaction pathway and sets the barrier for the whole process from **2**-Me to **4**-Me (20.9 kcal mol^{-1} above **2**-Me). Views of the DFT-optimised structures of **B**-Me and of the transition state **TS1** are given in Figure 5.

The N1-Re-N3 bond angle increases by 14° upon progression from **A**-Me to **TS1** and the carbene ligand moves by about 30° from its *trans* position (C1-Re-N3 = 159.5° for **TS1**). In the DFT-optimised structures of **A**-Me, **TS1** and **B**-Me the changes in the intermolecular distances N1–C1 of 2.87, 2.19 and 1.41 Å, respectively, reveal a relatively early transition state for the coupling process. The product **B**-Me may be best described as an azaketene ligand that can rearrange from C=N metal binding (**B**-Me, −10.5 kcal mol^{-1}) to N=O coordination (**C**-Me, −49.0 kcal mol^{-1}). Such an isomerisation process seems plausible, as a large number of stable oximate complexes with N,O attachment are known.[16] The isomerisation is accompanied by only a small activation barrier of **TS2** ($\Delta\Delta E_0^{\neq} = +12.3$ kcal mol^{-1}), but is very exothermic, with $\Delta\Delta E_0 = -38.5$ kcal mol^{-1}. The optimised η^1-structure of **TS2** (Figure 5) reveals a very long Re–C1 distance of 2.78 Å with the C1 atom almost sp^2 hybridised.

The heteroene-type reaction step includes the cleavage of the NO bond, previously elongated and weakened by interaction of the oxygen atom with the metal centre (N–O = 1.23 and 1.35 Å for **B**-Me and **C**-Me, respectively). The model complex **3**-Me is tremendously stabilised in energy relative to all previous key intermediates: the mass-balanced relative energies are $\Delta E_0 = -102.1$ kcal mol^{-1} with respect to **2**-Me and $\Delta\Delta E_0 = -53.1$ kcal mol^{-1} with respect to **C**-Me. The rhenium centre is in a stable pseudooctahedral environment and the two *trans* nitrile ligands in **3**-Me contribute strongly to the high stability of the complex. The slow transformation of **3a** and **3b** into **4a** and **4b** can be considered as a nucleophilic attack of the imino function on the carbon atom of the benzonitrile ligand accompanied by a prototropic rearrangement of the imino proton. Both these processes have been simulated, leading successively from **3**-Me to **D**-Me and from **D**-Me to **4**-Me, and have been calculated to be exothermic by 9.7 and 12.6 kcal mol^{-1}, respectively.

Alternatively, the NO insertion was also studied, starting directly from **2**-Me instead of **A**-Me, eliminating any influence of acetonitrile in the coordination sphere. The relative energies of the optimised stationary points **TS1**′ and **B**′-Me (for geometries, see Figure S1 in the Supporting Information) corresponding to the first step of the insertion revealed an energetically unfavourable pathway. The acetonitrile-free analogue of **B**-Me, **B**′-Me, is higher in energy by $\Delta E_0 = +23.2$ kcal mol^{-1} and its formation has a much higher energetic barrier of $\Delta E_0^{\neq} = +42.2$ kcal mol^{-1} (**TS1**′). Although these computational results for the PMe_3 model systems strongly support the given mechanism of Scheme 1, alternative reaction pathways cannot be excluded completely. Indeed, the first step after addition of an acetonitrile molecule to **2a** and **2b** would be rate determining. Therefore, evaluation of alternatives to the **TS1** route would be appropriate. For instance attack of an acetonitrile molecule on the metal centre of **A**′-Me or on the carbene ligand of **A**-Me are conceivable. The energy difference between these isomers could actually be reduced from $\Delta E_0 = 6.0$ kcal mol^{-1} to $\Delta E_{sol} = 2.0$ kcal mol^{-1} by applying a solvation model. Both reactions would result in the same product **E**-Me (Figure 6). Interestingly, a simple rotation of the alkyl group, during which the acetonitrile approaches the equatorial plane,

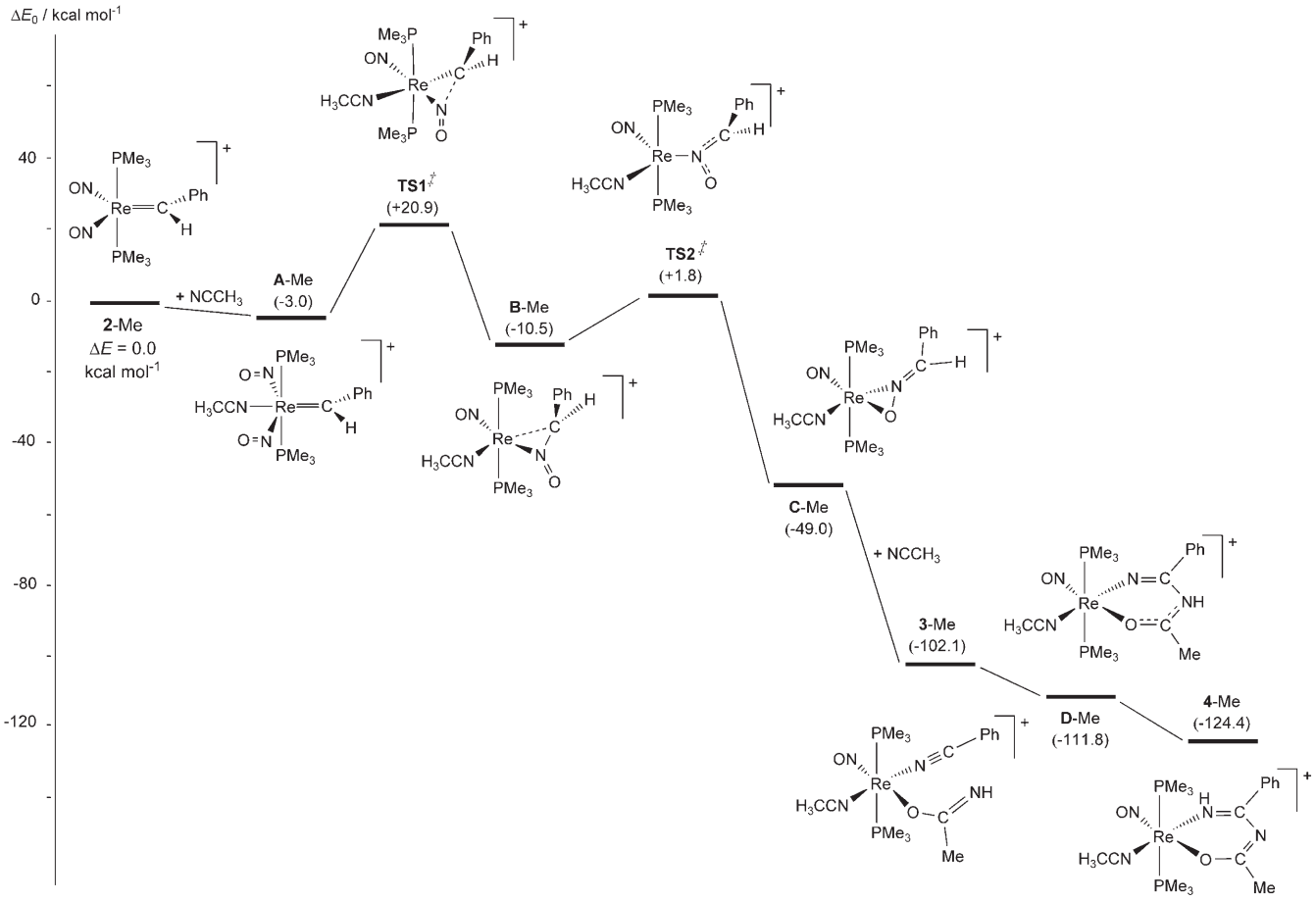


Figure 4. Calculated reaction pathway with electronic energies (ΔE_0 in kcal mol^{-1}) relative to compound **2**-Me taken as reference.

could lead to a direct migration of one NO group onto the carbon atom of the nitrilium unit core to form the 5-membered ring species **F**-Me (Figure 6).

According to the calculated energy of **F**-Me ($\Delta E_0 = -39.1$ kcal mol^{-1}), the formation of this species would be plausible, but its involvement in the mechanism can be ruled out for several reasons. Chemically, the final product **4** would necessitate a nucleophilic attack of the nitrogen atom on the weakly metal-bound carbon atom across the ring system, leading to a four-membered heterocycle. Such a reaction step would generate a highly strained ligand system, which would require the elimination of acetonitrile from the heterocycle in a further step to generate **B**-Me, and is, therefore, unlikely. Furthermore, due to its relative thermodynamic stability, **F**-Me would mark a thermodynamic drop in this reaction sequence and one would expect to be able to detect intermediates of this kind. However, our spectroscopic analysis revealed no such intermediates, rather, the almost quantitative formations of **3a** and **3b** and **4a** and **4b** were detected. Finally, the calculations revealed that the coordination of a second acetonitrile molecule is energetically unfavourable at **A**-Me by 14.7 kcal mol^{-1} and at **A′**-Me by 8.7 kcal mol^{-1}. The calculated energies, including solvation, even raise these energies to 16.7 and 14.7 kcal mol^{-1}, respectively. Furthermore, the Gibbs free energy of **E**-Me is +34.3 kcal mol^{-1}, which is calculated to be even higher than the Gibbs free energy of +32.9 kcal mol^{-1} calculated for **TS1**, the first transition state of the NO insertion pathway described. Thus, we can assume that the alternative-pathway species, such as **F**-Me, cannot be formed during the reaction, as coordination of a second acetonitrile molecule is less favourable.

Conclusion

We describe a unique reaction sequence in the ligand sphere of complexes **2a** and **2b**, in which a coordinated nitrosyl ligand, a carbene unit and an acetonitrile molecule were transformed into a (1*Z*)-*N*-[imino(phenyl)methyl]ethanimidate ligand. Experimental observations with concomitant DFT calculations allowed us to describe this unique reaction sequence on a mechanistic level, and confirmed that the pathway first involved the direct migratory insertion of the nitrosyl ligand into the benzylidene ligand, leading to a short-lived oximate species. In a further step, a pericyclic heteroene-type reaction between the azaketenate ligand in **C** and an acetonitrile molecule is anticipated to yield direct-

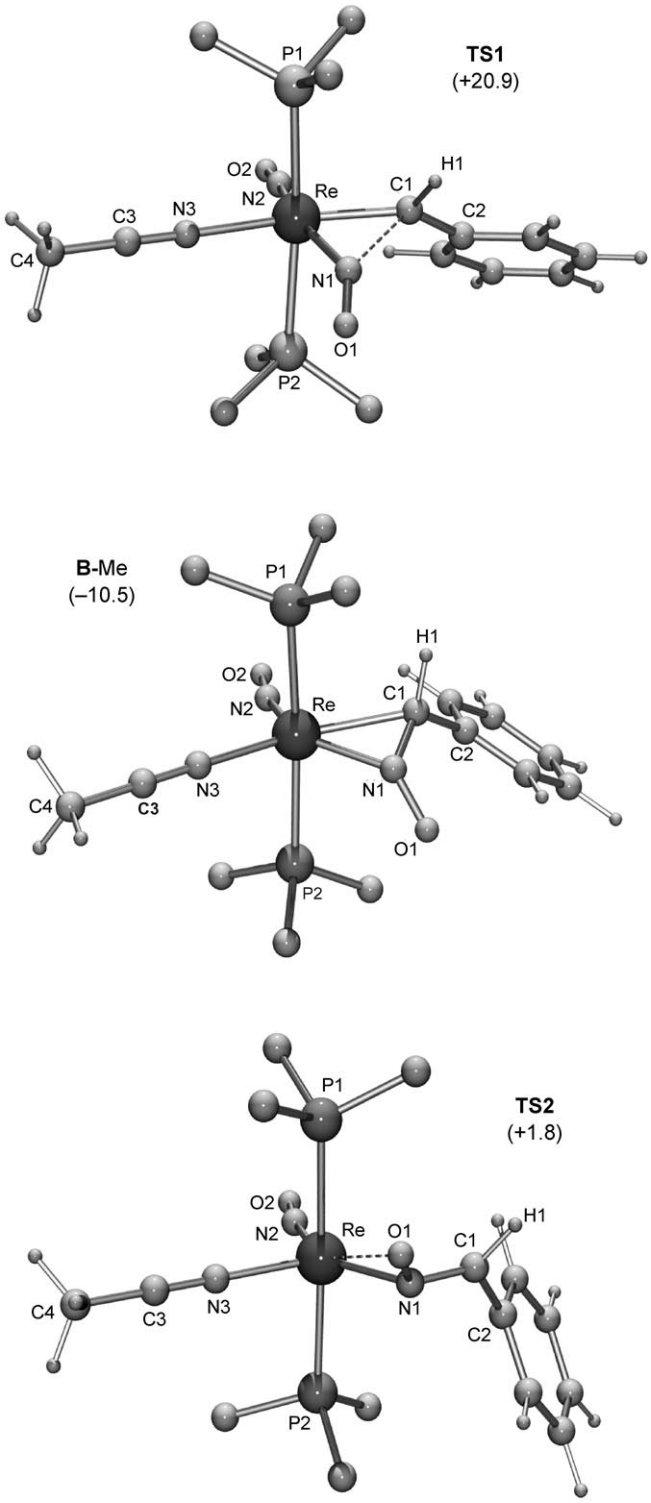


Figure 5. DFT-optimised structures and relative energies of **TS1**, **B**-Me and **TS2**. Important geometrical parameters are as follows. **TS1**: Re–C1 = 2.10, Re–N1 = 2.02, Re–N2 = 1.81, N1–O1 = 1.19, N1···C1 = 2.19 Å; Re-N1-O1 = 144.8, N1-Re-C1 = 64.4, N2-Re-C1 = 99.2, N3-Re-C1 = 159.5°. **B**-Me: Re–C1 = 2.25, Re–N1 = 2.02, Re–N2 = 1.78, N1–C1 = 1.41, N1–O1 = 1.23 Å; Re-N1-O1 = 140.1, N1-Re-C1 = 38.0°. **TS2**: Re···C1 = 2.78, Re–N1 = 2.10, Re–N2 = 1.78, N1–C1 = 1.33, N1–O1 = 1.27 Å; Re-N1-C1 = 106.1, Re-N1-O1 = 115.2°.

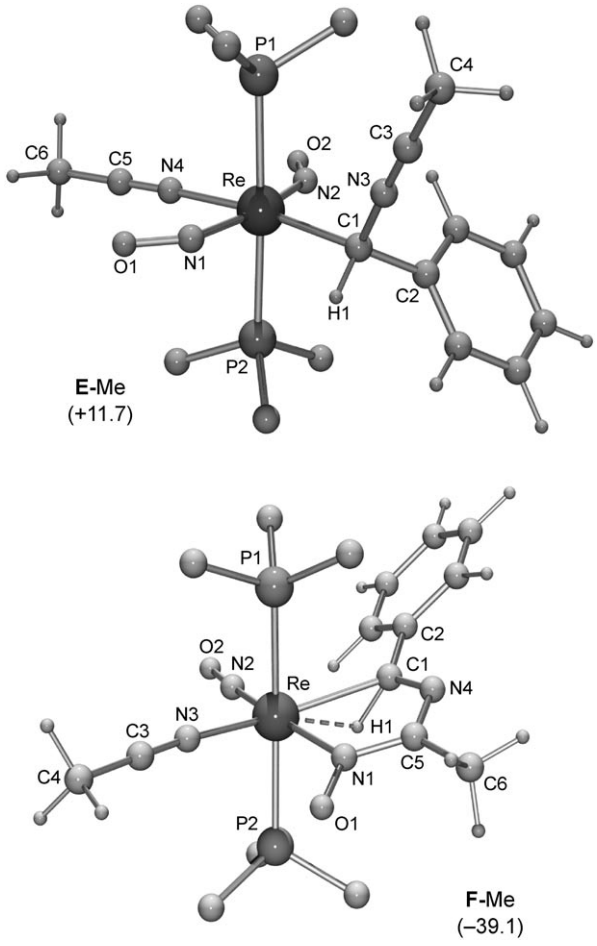


Figure 6. DFT-optimised structures and relative energies of **E**-Me and **F**-Me. Important geometrical parameters are as follows. **E**-Me: Re–C1 = 2.27, Re–N1 = 1.93, Re–N2 = 1.88, N1–O1 = 1.20, N2–O2 = 1.19 Å; Re-N1-O1 = 141.0, Re-N2-O2 = 146.6°. **F**-Me: Re–C1 = 2.38, Re–N1 = 2.11, Re–N2 = 1.79, N1–O1 = 1.28, N1–C5 = 1.34, C5–N4 = 1.35, C1–N4 = 1.31 Å; Re-C1-H1 = 51.1, Re-N1-O1 = 120.7, N1-Re-C1 = 72.1°.

ly the complexes **3a** and **3b**. The conversion of **3a** and **3b** into **4a** and **4b** involves a nucleophilic attack of the imino group onto the $C_{benzonitrile}$, followed by a 1,2-H shift.

Experimental Section

General: All synthetic operations were conducted in oven-dried glassware by 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. $[D_2]MeCl_2$ was purchased from Armar, stored in a Schlenk tube (Teflon tap) over P_4O_{10}, distilled and degassed prior to use. All chemicals were purchased from Aldrich or Fluka. Unless otherwise stated, all reagents were used without further purification. $[Re\{=CH(C_6H_5)\}(NO)_2(PR_3)_2][B\{m\text{-}C_6H_3(CF_3)_2\}_4]$ was prepared by following published methods.[9]

Physical measurements: Elemental analyses were performed by using a Leco CHNS-932 analysator at the University of Zürich, Switzerland. ^1H, ^{13}C, $^{31}P\{^1H\}$ and ^{15}N NMR data were recorded by using a Bruker Avance DRX500 spectrometer. Chemical shifts are expressed in parts per million

(ppm) referenced to CD_2Cl_2 or $[D_5]C_6H_5Cl$. All chemical shifts for $^{31}P\{^1H\}$ 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; d, doublet; t, triplet; m, multiplet; br, broad. Processing and analyses of the spectra were performed by using Bruker XWINNMR software. IR spectra were obtained by using KBr pellets or ATR methods with a Bio-Rad FTS-45 FTIR spectrometer.

Preparation of [Re(NCCH$_3$){NC(C$_6$H$_5$)}(NO){OC(CH$_3$)=NH}(PR$_3$)$_2$][B-{*m*-C$_6$H$_3$(CF$_3$)$_2$}$_4$] with R = Cy (3a) and R = *i*Pr (3b): Approximately 15 mL of acetonitrile was added to a solution of about ≈50 mg of **2** (≈0.03 mmol) in 1 mL of methylene chloride and kept at −30 °C for 24 h. The colour turned from dark-red to orange. After the disappearance (monitored by $^{31}P\{^1H\}$ NMR spectroscopy) of **2**, the solvent was removed under vacuum and the residue was washed with pentane (3×10 mL) and dried under vacuum. Yield 40.2 mg (90% for **3a**) and 45.2 mg (90% for **3b**).

Data for **3a**: ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.75–7.50 (m, 5H; NC(C_6H_5)), 4.14 (br s, 1H; OC(CH_3)=N*H*), 2.94 (s, 3H; NCCH_3), 2.34–1.92 (m, 66H; P(C_6H_{11})$_3$), 1.92 ppm (s, 3H; OC(CH_3)=NH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 177.4 (s, O*C*(CH$_3$)=NH), 139.0 (s, N*C*CH$_3$), 141.3, 132.0, 129.9, 126.2 (s, NC(C_6H_5)), 110.0 (s, N*C*(C_6H_5)), 28.2 (s, OC(*C*H$_3$)=NH) 34.6 (pseudo-t, J_{PC} = 10 Hz, P(C_6H_5)), 29.2, 27.9, 26.3 (s, P(C_6H_5)), 5.3 ppm (s, NC*C*H$_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −2.8 ppm (s, P(C_6H_{11})$_3$); ^{15}N NMR (CD_2Cl_2, 25 °C): δ = −213.4 (s, *N*CCH$_3$), −250.0 ppm (s, OC(CH$_3$)=*N*H); IR (KBr): $\tilde{\nu}$ = 2270 (w, NC), 2229 (w, NC), 1704 cm^{-1} (s, NO); elemental analysis calcd (%) for $C_{79}H_{90}BF_{24}N_4O_2P_2Re$: C 51.50, H 4.92, N 3.04; found: C 51.81, H 5.19, N 2.64.

Data for **3b**: ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.67–7.44 (m, 5H; NC(C_6H_5)), 4.15 (br s, 1H; OC(CH_3)=N*H*), 2.90 (s, 3H; NCCH_3), 2.56 (m, 6H; P{C*H*-(CH_3)$_2$}), 1.85 (s, 3H; OC(CH_3)=NH), 1.29 ppm (m, 36H; P{CH(CH_3)$_2$}); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 177.8 (s, O*C*(CH$_3$)=NH), 138.9 (s, N*C*CH$_3$), 140.78, 132.2, 129.6, 126.4 (s, NC(C_6H_5)), 109.4 (s, N*C*(C_6H_5)), 27.9 (s, OC(*C*H$_3$)=NH) 24.0 (pseudo-t, J_{PC} = 11 Hz, P{*C*H(CH$_3$)$_2$}), 19.0, 18.0 (s, P{CH(*C*H$_3$)$_2$}), 5.1 ppm (s, NC*C*H$_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 6.12 ppm (s, *P*{CH(CH$_3$)$_2$}); ^{15}N NMR (CD_2Cl_2, 25 °C): δ = −215.0 (s, *N*CCH$_3$), −250.3 ppm (s, OC(CH$_3$)=*N*H); IR (KBr): $\tilde{\nu}$ = 2271 (w, NC), 2228 (w, NC), 1697 cm^{-1} (s, NO); MS (FAB): *m*/*z* (%): 980.0 (18) [*M*]$^+$, 939.0 (23) [*M*$^+$−NCCH$_3$], 897.9 (7) [*M*$^+$−2NCCH$_3$], 876.9 (235) [*M*$^+$−NCPh], 835.8 (34) [*M*$^+$−NCCH$_3$, NCPh], 699.6 (10) [*M*$^+$−PCy$_3$], 658.6 (100) [*M*$^+$−NCCH$_3$, PCy$_3$], 596.5 (62) [*M*$^+$−NCPh, PCy$_3$], 553.5 (100) [*M*$^+$−NCCH$_3$, NCPh, PCy$_3$], 512.0 (24) [*M*$^+$−2NCCH$_3$, NCPh, PCy$_3$]; elemental analysis calcd (5) for $C_{61}H_{65}BF_{24}N_4O_2P_2Re$: C 45.76, H 4.10, N 3.50; found: C 46.02, H 4.09, N 3.22.

Preparation of [Re(NCCH$_3$)(OC{CH$_3$}N*N*H{C$_6$H$_5$})(NO)(PR$_3$)$_2$] with R = Cy (4a) and R = *i*Pr (4b): A solution of about ≈50 mg of **2** (≈0.03 mmol) in 20 mL of methylene chloride was stirred at RT for two days. After completion of the reaction (monitored by $^{31}P\{^1H\}$ NMR spectroscopy), the solvent was removed under vacuum. After removal of the solvent under reduced pressure, the residue was washed with pentane (3×20 mL) and dried under vacuum. Yield 43.6 mg (95% for **4a**) and 49.6 mg (>99% for **4b**).

Data for **4a**: ^1H NMR (CD_2Cl_2, 25 °C): δ = 8.76 (br s, 1H; N*H*=C-(C_6H_5)N=C(CH$_3$)O), 7.85–7.54 (m, 5H; NH=C(C_6H_5)N=C(CH$_3$)O), 2.89 (s, 3H; NCCH_3), 2.36 (s, 3H; NH=C(C_6H_5)N=C(CH_3)O), 2.10–1.05 ppm (m, 66H; P(C_6H_{11})$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 176.9 (s, NH=(C_6H_5)N=*C*(CH$_3$)O), 163.6 (s, NH=*C*(C_6H_5)N=C(CH$_3$)O), 141.3 (s, N*C*CH$_3$), 140.9, 131.9, 129.1, 126.7 (s, NH=C(*C*$_6$H$_5$)N=C(CH$_3$)O), 34.6 (pseudo-t, J_{PC} = 10 Hz, P(C_6H_{11})$_3$), 29.8 (s, NH=C(C_6H_5)N=C(*C*H$_3$)O), 29.5, 28.2, 26.5 (s, P(C_6H_{11})$_3$), 4.9 ppm (s, NC*C*H$_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 3.9 ppm (s, *P*(C_6H_{11})$_3$); ^{15}N NMR (CD_2Cl_2, 25 °C): δ = −207.9 (s, *N*CCH$_3$), −163.5 ppm (s, NH=C(C_6H_5)*N*=C(CH3)O); IR (ATR): $\tilde{\nu}$ = 2271 (w, NC), 1696 cm^{-1} (s, NO); elemental analysis calcd for $C_{79}H_{90}BF_{24}N_4O_2P_2Re$: C 51.50, H 4.92, N 3.04: found: C 51.25, H 5.03, N 2.86.

Data for **4b**: ^1H NMR (CD_2Cl_2, 25 °C): δ = 8.78 (br s, 1H; N*H*=C-(C_6H_5)N=C(CH$_3$)O), 7.78–7.46 (m, 5H; NH=C(C_6H_5)N=C(CH$_3$)O), 2.94 (s, 3H; NCCH_3), 2.38 (m, 6H; P{C*H*(CH$_3$)$_2$}$_3$), 2.30 (s, 3H; NH=C-(C_6H_5)N=C(CH_3)O), 1.27 ppm (m, 36H; P{CH(CH_3)$_2$}$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 177.1 (s, NH=(C_6H_5)N=*C*(CH$_3$)O), 164.0 (s, NH=*C*-(C_6H_5)N=C(CH$_3$)O), 140.9 (s, N*C*CH$_3$), 135.2, 131.8, 129.3, 126.7 (s, NH=C(C_6H_5)N=C(CH$_3$)O), 29.6 (s, NH=C(C_6H_5)N=C(*C*H$_3$)O), 24.4 (pseudo-t, J_{PC} = 12 Hz, P{*C*H(CH$_3$)$_2$}$_3$), 19.3, 19.1 (s, P{CH(*C*H$_3$)$_2$}$_3$), 4.7 ppm (s, NC*C*H$_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 12.1 ppm (s, P{*C*H(CH$_3$)$_2$}$_3$); ^{15}N NMR (CD_2Cl_2, 25 °C): δ = −209.4 (s, *N*CCH$_3$), −163.9 ppm (s, NH=C-(C_6H_5)*N*=C(CH3)O); IR (ATR): $\tilde{\nu}$ = 2273 (w, NC), 1691 cm^{-1} (s, NO); elemental analysis calcd (%) for $C_{61}H_{65}BF_{24}N_4O_2P_2Re$: C 45.76, H 4.10, N 3.50; found: C 46.15, H 4.49, N 3.45.

X-ray structure analysis of 4b: Crystals of **4b** protected in hydrocarbon oil were selected for X-ray analysis by using a polarising microscope. A crystal of good quality was mounted on the tip of a glass fibre and was immediately transferred to the goniometer of an imaging-plate-detector system (Stoe IPDS diffractometer), in which it was cooled to 123(2) K by using an Oxford Cryogenic System. The crystal-to-image distance was set to 50 mm (θ_{max} = 30.26°). The φ-rotation scan mode was applied for data collection. For the cell parameter refinement, 7998 reflections were selected from the whole limiting sphere. A total of 56724 diffraction intensities were collected,[17] of which 18321 were unique (R_{int} = 0.0510) after data reduction. A numerical absorption correction[18] based on ten crystal faces was applied with FACEitVIDEO and XRED.[17] The structure was solved by direct methods in the noncentrosymmetric space group *P*1 by using the program SHELXS-97.[19] A centre of symmetry was detected by examination of the crystal packing in the three main directions of the unit cell: the atomic parameters had to be shifted by a = 0.372, b = 0.023 and c = 0.08 Å. Interpretation of the difference Fourier maps, preliminary plot generations and checking for higher symmetry were performed by using PLATON[20] and the implemented program LEPAGE.[21] The refinement (SHELXL-97)[22] was continued in space group $P\bar{1}$ by using anisotropic displacement parameters for all non-hydrogen atoms. Positions of hydrogen atoms were calculated after each refinement cycle (riding model), except for the imine hydrogen atom H3, which was found in a difference electron-density map and was refined with isotropic displacement parameters. The structural plot (Figure 1) was generated by using ORTEP.[23]

Computational details: All geometry optimisations, vibrational frequency, zero-point and single-point energy calculations were performed with the Gaussian 03 program package[24] by using the hybrid *m*PW1PW91 functional, which includes modified Perdew–Wang exchange and Perdew–Wang 91 correlation,[25] in conjunction with the Stuttgart/Dresden ECPs (SDD) basis set[26] for the Re centre, the standard 6–31G basis set[27] for the hydrogen atoms, and the polarised 6–31G(d) basis set[28] for the remaining atoms. Pure basis functions (5d, 7f) were used in all calculations. Geometries were fully optimised without symmetry constraints and transition-state structures were obtained by using the QST2 procedure.[29] The nature of the optimised structures, either minima or transition states, was verified by frequency calculations at the same level. These frequency analyses also provided the zero-point energy correction to convert the total energies E_e to ground state energies E_0, the thermal corrections to the total energy, enthalpy and Gibbs free energy (all of which include the zero-point energy). The solvent effect was investigated by single-point calculations on the optimised gas-phase geometries for all the intermediates and transition states by using the CPCM model,[30] which is an implementation of the conductor-like screening solvation model COSMO[31] in Gaussian 03. Benzene was chosen as solvent (dielectric constant ε = 2.247) with UAKS radii for the respective atoms (Re, P, O, N, C, H). The single-point total energies were also corrected with the gas-phase zero-point energies (E_{sol}).

CCDC 299908 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

Funding from the Swiss National Science Foundation (SNSF) and from the University of Zürich is gratefully acknowledged.

[1] a) D. St. C. Black, *Comprehensive Coordination Chemistry, Vol. 1* (Eds: R. D. Gillard, J. A. McCleverty), Pergamon, **1987**, p. 415; D. St. C. Black, *Comprehensive Coordination Chemistry, Vol. 6* (Eds: R. D. Gillard, J. A. McCleverty), Pergamon, **1987**, p. 155; b) L. S. Hegedus, *Coord. Chem. Rev.* **1998**, *168*, 49; L. S. Hegedus, *Coord. Chem. Rev.* **1998**, *175*, 159; c) K. N. Mitra, S.-M. Peng, S. Goswami, *Chem. Commun.* **1998**, 1685; d) P. Bandyopadhyay, D. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello, S. Han, *J. Am. Chem. Soc.* **1983**, *105*, 6327; e) B. K. Santra, G. A. Thakur, P. Ghosh, A. Pramanik, G. K. Lahiri, *Inorg. Chem.* **1996**, *35*, 3050; f) G. K. Lahiri, S. Goswami, L. R. Falvello, A. Chakravorty, *Inorg. Chem.* **1987**, *26*, 3365; g) J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154; *Angew. Chem. Int. Ed.* **1998**, *37*, 2046; h) M. Bruncko, T.-A. V. Khoung, K. B. Sharpless, *Angew. Chem.* **1996**, *108*, 453; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 454; i) S. D. Gray, J. L. Thorman, V. A. Adamian, K. M. Kadish, K. L. Woo, *Inorg. Chem.* **1998**, *37*, 1; j) Z. Li, R. W. Quan, E. N. Jacobsen, *J. Am. Chem. Soc.* **1995**, *117*, 5889.

[2] a) T.-Y. Luh, M.-K. Leung, K.-T. Wong, *Chem. Rev.* **2000**, *100*, 3187; b) T. Kondo, T. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205; c) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067; d) A. D. Dilman, S. L. Ioffe, *Chem. Rev.* **2003**, *103*, 733; e) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731; f) G. Y. Li, G. Zheng, A. F. Noonan, *J. Org. Chem.* **2001**, *66*, 8677; g) N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 5553; h) E. J. Kuhlmann, J. J. Alexander, *Coord. Chem. Rev.* **1980**, *33*, 195; i) F. Diederich, P. J. Stang, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, **1998**; j) B. Cornils, W. A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, **1996**; k) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, Wiley-VCH, Weinheim, **1998**; l) P. C. Wailes, H. Weigold, A. P. Bell, *J. Organomet. Chem.* **1972**, *34*, 155; m) G. Fochi, C. Floriani, A. Chiesi-Villa, C. Gaustini, *J. Chem. Soc. Dalton Trans.* **1986**, 445; n) C. J. Jones, J. A. McCleverty, A. S. Rothin, *J. Chem. Soc. Dalton Trans.* **1985**, 405; o) A. R. Middleton, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1981**, 1898; p) A. J. Shortland, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1973**, 872.

[3] a) G. B. Richter-Addo, P. Legzdins, *Metal Nitrosyls*, Oxford University Press, New York, **1992**; b) M. Cameron, B. G. Gowenlock, G. Vasapollo, *Chem. Soc. Rev.* **1990**, *19*, 355; c) G. B. Richter-Addo, P. Legzdins, *Chem. Rev.* **1988**, *88*, 991; d) F. Bottomley in *Reactions in Coordinated Ligands, Vol. 2* (Ed.: P. S. Braterman), Plenum, New York, **1989**, pp. 115; e) K. K. Pandey, *Coord. Chem. Rev.* **1983**, *51*, 69; f) J. Chang, D. M. Seidler, R. G. Bergman, *J. Am. Chem. Soc.* **1989**, *111*, 3258; g) E. B. Brouwer, P. Legzdins, S. J. Rettig, K. J. Ross, *Organometallics* **1994**, *13*, 2088; h) W. P. Weiner, R. G. Bergman, *J. Am. Chem. Soc.* **1983**, *105*, 3922; i) W. P. Weiner, M. A. White, R. G. Bergman, *J. Am. Chem. Soc.* **1981**, *103*, 3612; j) M. D. Seidler, R. G. Bergman, *Organometallics* **1983**, *2*, 1897; k) M. D. Seidler, R. G. Bergman, *J. Am. Chem. Soc.* **1984**, *106*, 6110; l) B. N. Diel, *J. Organomet. Chem.* **1985**, *284*, 257; m) P. Legzdins, B. Wassink, F. W. B. Einstein, A. A. Willis, *J. Am. Chem. Soc.* **1986**, *108*, 317; n) A. Goldhaber, K. P. C. Vollhart, E. C. Walborsky, M. Wolfgruber, *J. Am. Chem. Soc.* **1986**, *108*, 516; o) A. R. Middleton, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1980**, 1888; p) S. Niu, B. Hall, *J. Phys. Chem. A* **1997**, *101*, 1360; q) S. Niu, B. Hall, *J. Am. Chem. Soc.* **1997**, *119*, 3077.

[4] D. Forster, T. W. Dekleva, *J. Chem. Educ.* **1986**, *63*, 204.

[5] R. F. Heck, D. S. Breslow, *J. Am. Chem. Soc.* **1961**, *83*, 1961.

[6] Recent reviews: a) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675; b) P. Dembech, G. Seconi, A. Ricci, *Chem. Eur. J.* **2000**, *6*, 1281; c) B. H. Yang, S. L. Buchwald, *J. Organomet. Chem.* **1999**, *576*, 125.

[7] H. Klein, H. Karsch, *Chem. Ber.* **1976**, *109*, 1453.

[8] a) W. A. Herrmann, *Angew. Chem.* **1978**, *90*, 855; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 800; b) T. W. Bodnar, A. R. Cutler, *J. Am. Chem. Soc.* **1983**, *105*, 5926; c) M. A. Gallop, W. R. Roper, *Adv. Organomet. Chem.* **1988**, *25*, 121; d) P. Schwab, N. Mahr, *Angew. Chem.* **1993**, *105*, 1498; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1480; e) H. Werner, *J. Organomet. Chem.* **1995**, *500*, 331; f) E. Bleuel, M. Laubender, B. Weberndörfer, H. Werner, *Angew. Chem.* **1999**, *111*, 222; *Angew. Chem. Int. Ed.* **1999**, *38*, 156; g) D. B. Grotjahn, G. A. Bikzhanova, L. B. S. Collins, T. Concolino, K. C. Lam, A. L. Rheingold, *J. Am. Chem. Soc.* **2000**, *122*, 5222.

[9] C. M. Frech, O. Blacque, H. W. Schmalle, H. Berke, C. Adlhart, P. Chen, *Chem. Eur. J.* **2006**, *12*, 3325.

[10] R. Beckhaus, I. Strauss, T. Wagner, *Angew. Chem.* **1995**, *107*, 738; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 688.

[11] G. La Monica, M. Freni, S. Cenini, *J. Organomet. Chem.* **1974**, *71*, 57.

[12] C. M. Frech, A. Llamazares, M. Alfonso, H. W. Schmalle, H. Berke, *Russ. Chem. Bull.* **2004**, *113*, 53, 1116.

[13] a) B. Desai, T. N. Danks, G. Wagner, *J. Chem. Soc. Dalton Trans.* **2004**, 166; b) Y. Yu, M. Ohno, S. Eguchi, *J. Chem. Soc. Chem. Commun.* **1994**, 331; c) Y. Yu, N. Watanabe, M. Ohno, S. Eguchi, *J. Chem. Soc. Perkin Trans. 1* **1995**, *11*, 1417; d) Y. Yu, H. Fujita, M. Ohno, S. Eguchi, *Synthesis* **1995**, 498; e) L. A. G. M. van den Broek, *Tetrahedron* **1996**, *52*, 4467; f) H. Sang, E. G. Janzen, L. Poyer, *J. Chem. Soc. Perkin Trans. 2* **1996**, 1183; g) R. Plate, P. H. H. Hermkens, J. M. M. Smits, R. J. F. Nivard, H. C. J. Ottenheijm, *J. Org. Chem.* **1987**, *52*, 1047; h) J. M. M. Smits, P. T. Beurskens, J. R. M. Smits, R. Plate, H. Ottenheijm, *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 15; i) L. Eberson, C. M. Hartshorn, M. P. Hartshorn, J. J. McCullough, *Synth. Commun.* **1997**, *27*, 3779; j) L. Eberson, J. J. McCullough, C. M. Hartshorn, M. P. Hartshorn, *J. Chem. Soc. Perkin Trans. 2* **1998**, *1*, 41; k) G. Wagner, M. Haukka, J. J. R. Frausto da Silva, A. J. L. Pombeiro, V. Y. Kukushkin, *Inorg. Chem.* **2001**, *40*, 264; l) G. Wagner, J. J. R. Frausto da Silva, A. J. L. Pombeiro, V. Y. Kukushkin, *J. Am. Chem. Soc.* **2000**, *122*, 3106.

[14] a) M. Stratakis, M. Orfanopoulos, C. S. Foote, *J. Org. Chem.* **1998**, *63*, 1315; b) M. Stratakis, M. Hatzimarinaki, G. E. Froudakis, M. Orfanopoulos, *J. Org. Chem.* **2001**, *66*, 3682; c) M. Yamanaka, K. Mikami, *Helv. Chim. Acta* **2002**, *85*, 4264; d) M. J. Wanner, G.-J. Koomen, *J. Chem. Soc. Perkin Trans. 1* **2001**, 1908.

[15] It should be mentioned that an alternative, but less-plausible pathway with respect to the pericyclic heteroene reaction could be operative in the transformation of intermediate **C** into **3a** and **3b**. By anticipating a 1,3-H shift in **C** accompanied by breaking of the N−O bond, the benzonitrile hydroxo complex $[Re(NO)(PR_3)_2(NCCH_3)(NCC_6H_5)(OH)]^+$ would be formed. A proton transfer from the hydroxy ligand to a second acetonitrile molecule followed by a nucleophilic attack of the oxo group on the carbon atom of the thereby-activated acetonitrile molecule could lead to **3a** and **3b**.

[16] a) M. K. Mahanthappa, A. P. Cole, R. M. Waymouth, *Organometallics* **2004**, *23*, 1405; b) P. Barrio, M. A. Esteruelas, E. Onate, *Organometallics* **2003**, *22*, 2472; c) H. Werner, T. Daniel, M. Mueller, N. Mahr, *J. Organomet. Chem.* **1996**, *512*, 197; d) A. Proust, P. Gouzerh, F. Robert, *J. Chem. Soc. Dalton Trans.* **1994**, *6*, 825; e) H. Werner, T. Daniel, W. Knaup, O. Nuernberg, *J. Organomet. Chem.* **1993**, *462*, 309; f) U. Meyer, H. Werner, *Chem. Ber.* **1990**, *123*, 697; g) R. B. King, K. N. Chen, *Inorg. Chem.* **1977**, *16*, 1164; h) G. P. Khare, R. J. Doedens, *Inorg. Chem.* **1977**, *16*, 907.

[17] Stoe IPDS software for data collection, cell refinement, and data reduction: Version 2.92, Stoe, Darmstadt, Germany, **1999**.

[18] P. Coppens, L. Leiserowitz, D. Rabinovich, *Acta Crystallogr.* **1965**, *18*, 1035.

[19] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[20] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[21] Y. Le Page, *J. Appl. Crystallogr.* **1987**, *20*, 264.

[22] G. M. Sheldrick, *SHELXL-97: Software Package for Crystal Structure Determination and Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

[23] C. K. Johnson, ORTEPII, Report ORNL-5138, Oak.

[24] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N.

Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, Nakai, H. M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[25] a) C. Adamo, V. Barone, *J. Chem. Phys.* **1998**, *108*, 664; b) J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* **1996**, *54*, 16533; c) K. Burke, J. P. Perdew, Y. Wang in *Electronic Density Functional Theory: Recent Progress and New Directions* (Eds.: J. F. Dobson, G. Vignale, M. P. Das), Plenum, New York, **1998**.

[26] D. Andrae, U. Haussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123.

[27] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.

[28] P. C. Hariharan, J. A. Pople, *Chem. Phys. Lett.* **1972**, *16*, 217.

[29] a) C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comput. Chem.* **1996**, *17*, 49; b) C. Peng, H. B. Schlegel, *Isr. J. Chem.* **1994**, *33*, 449.

[30] a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995; b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669.

[31] a) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 1* **1993**, *2*, 799; b) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224; c) A. Klamt, V. Jonas, *J. Chem. Phys.* **1996**, *105*, 9972.

Received: March 1, 2006
Published online: May 16, 2006

