Insertion and Cycloaddition Reactivity of a Transition-Metal *N*-Metalloimine**

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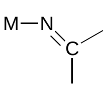
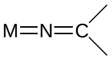
Dedicated to Professor Maurice Brookhart on the occasion of his 60th birthday

The presence of electron-releasing main-group-metal substituents on the nitrogen atom increases the reactivity of imines **A** towards dipolar reagents such as isocyanates[1] and ketenes.[2] We speculated that, in addition to this inductive effect, a low-oxidation transition-metal substituent would contribute a destabilizing interaction between the lone pair on the nitrogen atom and the filled metal d orbitals.[3] However, all structurally characterized $M(N{=}CR_2)$ complexes have essentially linear M-N-C geometries[4] as a result of π donation of the lone pair on the nitrogen atom to empty metal orbitals. Thus, these azavinylidene[5] complexes **B** are more related to alkylideneammonium cations than to imines.[6]



A



B

Herein we report the synthesis, structure, and a preliminary account of the reactivity of an *N*-metalloimine (type **A**) which contains a transition-metal fragment.

The reaction of $KN{=}CPh_2$ with $[Re(OTf)(CO)_3(bpy)]$ (bpy = 2,2′-bipyridine) afforded the complex $[Re(N{=}CPh_2)(CO)_3(bpy)]$ (**1**), which was characterized spectroscopically and by X-ray diffraction (Figure 1 a). For comparison, the structure of the imine complex $[Re(HN{=}CPh_2)(CO)_3(bpy)]^+$ (**2**), synthesized as its triflate salt by reaction of **1** with HOTf, was also determined (Figure 1 b). The Re-N-C angle (133.9(4)°) for the alkylideneamido group of **1**, even smaller than the Re-N-C angle (138.9(2)°) of **2**, indicates the absence of N-to-Re π donation. The larger deviations from linearity in previously known azavinylidene complexes (152.9(4)° and 157.2(4)° for $[OsCl({=}N{=}CMe_2)({\equiv}CCH_3)(PiPr_3)_2][OTf]$[7] and $[OsCl({=}N{=}CMe_2)({=}CHPh)(PiPr_3)_2]$,[8] respectively) can be related to the presence of bulky ancillary ligands, whereas such effects are absent in **1**. The $Re{-}NCPh_2$ distance (2.113(4) Å) in **1** is comparable to the $Re{-}N(H)CPh_2$ distance (2.192(3) Å) in **2**, which is in agreement with the lack of multiple-bond character of the Re–N bond.[9]

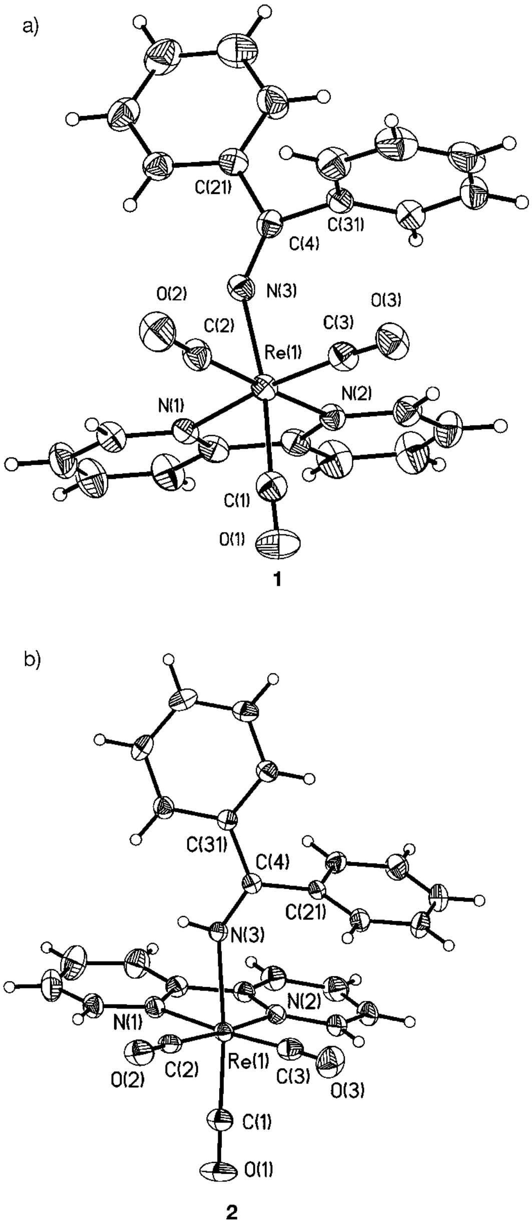


Figure 1. Thermal ellipsoid (30 %) plots of **1** (a) and **2** (b). See Supporting Information for further details.

Despite the structural similarity, the spectroscopic data of **1** and **2** are very different. Values of ν_{CO} even lower than those found for the related alkoxo[10] and amido[11] complexes reflect the strongly donor character of the alkylideneamido ligand in the neutral complex **1**, whereas the higher wavenumbers of **2** are consistent with its cationic nature. ^{13}C NMR spectroscopy data indicate that the two phenyl groups of **1** are equivalent. Given the angular geometry of the alkylideneamido group, this should result from a fast exchange of the position of the metal atom between the two electron pairs at the alkylideneamido nitrogen atom.[12]

Complex **1** acts as a nucleophile towards isocyanates. Thus, its reactions with RNCO (R = Ph, *p*Tol; Scheme 1) afford the products (**3** and **4**, respectively) of formal isocyanate insertion

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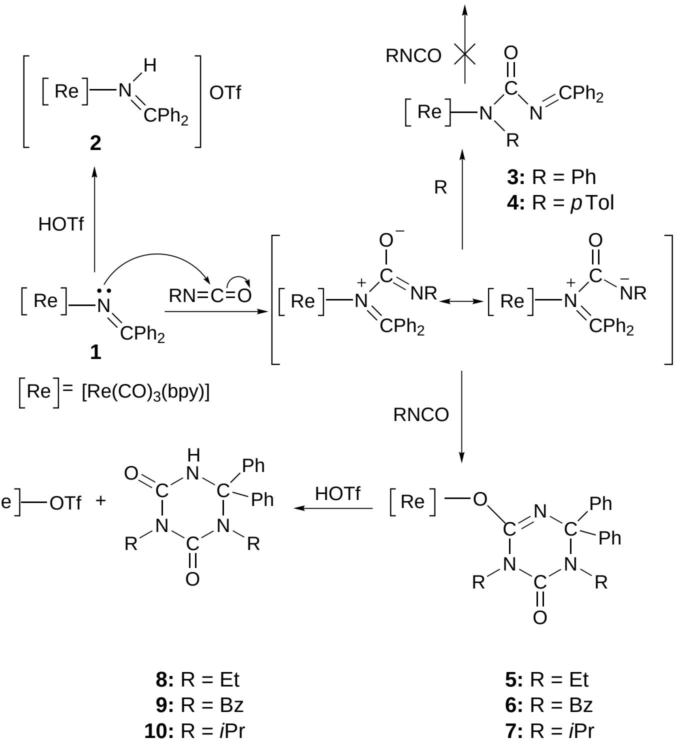
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Reaction of complex **1** as a nucleophile with isocyanates

into the Re–N bond, as confirmed by an X-ray crystal structure determination of **4** (Figure 2a). This parallels the proposed first step of the reactions of isocyanates towards either late-transition-metal nucleophilic amido complexes[13] or N-silylimines.[1,14] The rhenaimine **1** is more reactive than *N*-silylimines; the reaction with arylisocyanates, instantaneous at room temperature with **1**, takes 8 h with $Me_3SiN{=}C(H)Ph$.[1]

Complex **1** reacts with 2 equivalents of alkylisocyanates, as shown in Scheme 1. The products (**5**, **6**, and **7**) were characterized spectroscopically and (for **6**) by X-ray diffraction (see Figure 2b). The six-membered cyclic ligands present in **5**–**7** should result from [4+2] cycloaddition of a second molecule of RNCO to the 1,3-diaza-1,3-butadiene moiety formed in a previous step of formal RNCO insertion into the Re–N bond, similar to that leading to the formation of compounds **3**–**4**. Attempts to detect the proposed intermediate were unsuccessful, and only mixtures of **5**–**7** and unreacted **1** were obtained in the reaction of equimolar amounts of **1** and alkyl isocyanates.

Compounds **3** and **4** are unreactive (12 h in refluxing THF) towards either PhNCO or EtNCO. We suspect that the formation of the intermediate 1,3-azabutadiene required for the cycloaddition to take place is precluded for R = aryl by the stability of the Re–N species **3** and **4**.

The reactions of **5**–**7** with HOTf cleanly demetalate the 1,3,5-triazine-2,4-diones and allow an efficient recycling of the metal auxiliary as the triflato complex $[Re(OTf)(CO)_3(bpy)]$ (Scheme 1).

In summary, we have unambiguously characterized a transition-metal *N*-metalloimine; that is, an alkylideneamido complex that is *not* an azavinylidene.[15] Accordingly, the nucleophilicity of the nitrogen atom dominates its reactivity. Studies of the reactivity of **1** towards ketenes are in progress in our laboratories.

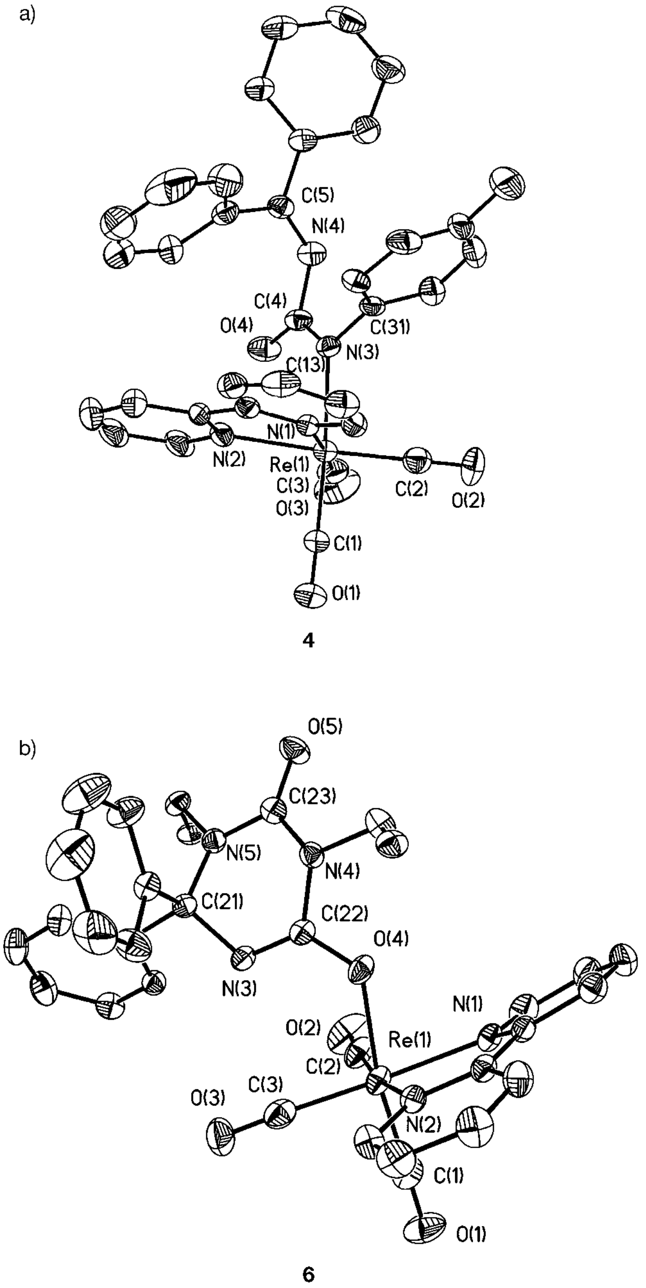


Figure 2. Thermal ellipsoid (30 %) plots of **4** (a) and **6** (b)(phenyl rings on the benzyl groups are omitted for clarity). See Supporting Information for further details.

Experimental Section

All manipulations were performed under a nitrogen atmosphere by using Schlenk techniques. Correct C, H, N analyses were obtained for all the new complexes. Full experimental details can be found in the Supporting Information. CCDC-184784–184787 contain the supplementary crystallographic data for the structures reported in this paper (**1**, **2**, **4**, and **6**, respectively). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk)

1: A solution of K[NCPh$_2$] (0.094 mmol) in THF (10 mL) was transferred to a solution of [Re(OTf)(CO)$_3$(bpy)] (0.050 g, 0.086 mmol) in THF (15 mL) at −78 °C. The color changed from yellow to dark green. After reaching room temperature, 15 min stirring, solvent evaporation, extraction (CH$_2$Cl$_2$, 2 × 10 mL), filtration, evaporation of the solvent, crystallization from THF/hexane yielded **1** in (0.045 g, 87 %). IR (THF): $\tilde{\nu} = 1999$, 1898, 1880 cm^{-1}; ^{1}H NMR(200 MHz, CD$_2$Cl$_2$): $\delta = 8.80$, 8.37, 8.11, 7.44 (m, 2H each; bpy), 7.24 (m, 6H; Ph), 6.96 ppm (m, 4H; Ph); ^{13}C{^{1}H} NMR (75.46 MHz, CD$_2$Cl$_2$): $\delta = 158.10$ [N=C], 157.14, 155.30, 143.25 [bpy], 142.30, 128.94, 127.53, 126.14 [2Ph], 125.54, 121.79 ppm [bpy].

Reaction of 1 with *p*TolNCO: *p*TolNCO (9.0 μL, 0.082 mmol) was added to a solution of **1** (0.050 g, 0.082 mmol) in THF (15 mL). Evaporation of the solvent, followed by crystallization from CH$_2$Cl$_2$/hexane yielded **4** (0.053 g, 87 %). IR (CH$_2$Cl$_2$): $\tilde{\nu} = 2014$, 1913, 1887, 1716 cm^{-1} (C=O); ^{1}H NMR(200 MHz, CD$_2$Cl$_2$): $\delta = 8.80$, 8.74, 8.16 (m, 2H each; bpy), 7.54–7.05 (m, 24H; bipy, Ph), 6.66, 6.64, 6.51, 6.48 (qAA′BB′, 4H; *p*Tol), 2.05 ppm (s, 3H; CH$_3$, *p*Tol).

Reaction of 1 with BzNCO: BzNCO (20 μL, 0.164 mmol) was added to a solution of **1** (0.050 g, 0.082 mmol) in THF (15 mL) and the mixture was stirred for 15 min. Workup as for **4** afforded orange crystals of **6** (0.060 g, 84 %). IR (THF): $\tilde{\nu} = 2019$, 1917, 1890, 1669, 1623 cm^{-1} (C=O and C=N); ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 8.83$, 7.84, 7.75 (m, 2H each; bpy), 7.39–6.79 (m, 44H; bpy, Bz, Ph), 4.49 (s, 2H, CH$_2$), 4.29 ppm (s, 2H; CH$_2$).

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An Iridaborane Reaction Cycle Driven by PMe$_3$ and BH$_3$·THF: Synthesis and Characterization of [Cp*IrB$_3$H$_7$(PMe$_3$)] and [Cp*IrB$_2$H$_6$(PMe$_3$)]**

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Polyhedral boron-containing compounds show an extensive structural chemistry that exhibits clear interconnections with organometallic and other p-block transition-element compounds.[1,2] However, until recently, limitations of synthetic methods have precluded systematic study of metallaboranes, and as a result their reactivity has remained largely unexplored relative to that of organometallic compounds.[3–6] This changed significantly with the development of a general route to a class of metallaboranes in which the metal can be varied from Group 5–9.[7] The results to date show that although metallaborane chemistry does overlap with organometallic chemistry, the former exhibits reactivities without parallel in other areas.[8,9]

The chemistry of the environment and of living organisms is often reversible and based on catalytic and stoichiometric cycles. Industrial chemistry is also highly reliant on the use of catalytic and stoichiometric cycles. The importance of such systems has provided much of the impetus for research in organometallic chemistry.[10,11] Even though significant examples exist,[12–14] polyhedral boron chemistry shows a marked lack of reaction cycles either catalytic or stoichiometric. Herein we report a novel stoichiometric cycle in which the iridaboranes, [1-(Cp*)-1-(H)$_2$-*arachno*-1-IrB$_3$H$_7$] (**1**)[15] and [1-(Cp*)-1-H-*arachno*-1-IrB$_4$H$_9$] (**2**)[15] (Cp* = η^5-C$_5$Me$_5$) are interconverted via novel phosphane-substituted derivatives (Scheme 1). The chemistry is driven by acid/base chemistry of PMe$_3$ (Me = CH$_3$) and borane.

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