A new route for the synthesis of an alkylideneamido complex†

Luciano Cuesta,‡[a] Dolores Morales,[a] Julio Pérez*[a] and Daniel Miguel[b]

Received (in Montpellier, France) 31st January 2008, Accepted 13th March 2008
First published as an Advance Article on the web 2nd April 2008
DOI: 10.1039/b801799a

The synthesis of the new alkylideneamido complex [Re{N=C(Ph)C≡CPh}(CO)$_3$(bpy)] is described. Analysis of its spectroscopic and structural data reveals the absence of π-donation from the nitrogen to the metal.

The vast majority of the mononuclear structurally-characterized M(N=CR$_2$) complexes display close to linear M–N–C geometries as a result of the existence of significant π-donation from the nitrogen atom to the empty metal orbitals. In analogy with vinylidene complexes, they have been aptly termed azavinylidenes (**A**, Fig. 1).[1] Recently, we reported the synthesis of the metalloimine [Re(N=CPh$_2$)(CO)$_3$(bpy)] (**1**, bpy = 2,2′-bipyridine).[2] Complex **1** presents an angular M–N=CR$_2$ moiety, as in previously known alkylidene compounds (**B**, Fig. 1),[3] which are not azavinylidenes.

In contrast with azavinylidene complexes, the reactivity of **1**[2,4] is dominated by the strong nucleophilicity of the alkylideneamido nitrogen, and by the ability of the ligand to participate in insertion and cycloaddition processes; of particular interest are the reactions of *N*-rhenaimine **1** with isocyanates[2] and ketenes,[4a] which allowed us, after demetallation, to isolate, in high yield and in a straightforward manner, triazines and β-lactams, respectively. These results encouraged us to seek an alternative synthesis of new alkylideneamido complexes. The strategy employed for the synthesis of **1**, namely the reaction between [Re(OTf)(CO)$_3$(bpy)] and KN=CPh$_2$ (generated *in situ* by deprotonation of the benzophenone imine with K[N(SiMe$_3$)$_2$]), cannot be easily extended to the synthesis of new kinds of alkylideneamido complexes due to the fact that most *N*-unsubstituted Schiff bases, HN=CRR′, particularly those derived from aldehydes, or from ketones with non-aryl groups, are thermally unstable. The synthesis of ketimines by the reaction of organomagnesium or organolithium compounds with nitriles, and with subsequent hydrolysis, has been known since early in the last century.[5] We speculated that an analogous reaction, where quenching with a cationic metal fragment replaces the final protonation step (see Scheme 1), could allow us to synthesize new alkylideneamido species.

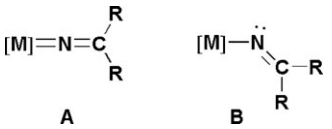
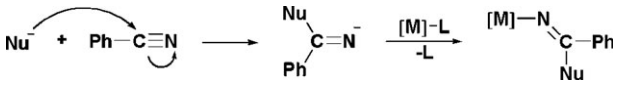


Fig. 1 Generic azavinylidene (**A**) and alkylideneamido (**B**) complexes.

In our initial efforts toward the synthesis of alkylideneamido complexes, we examined the reactions between Grignard or alkyl lithium reagents and benzonitrile, using the complex [Re(OTf)(CO)$_3$(bpy)] as the source of the metallic fragment in all cases. These reactions proved to be unproductive, affording in all cases complicated mixtures of products. The formation of these mixtures could be attributed to the operation of rearrangements, such as the one shown in the Scheme 2, which would cause the formation of amido species, in addition to the desired alkylideneamido complexes. This kind of hydrogen migration has been previously observed during complexation studies of lithium imides with α-C–H units attached to the C=N moiety.[6]

According to this observation, when 2-thienyllithium, which does not have C–H units susceptible to undergo the isomerization discussed above, was employed as a nucleophile, only one organometallic compound was obtained, the spectroscopic data (^{1}H NMR and IR) of which are consistent with the formation of alkylideneamido complex **2** (Fig. 2). Unfortunately, no satisfactory elemental analysis could be obtained, a fact that we attribute to the presence of the lithium triflate by-product. Thus, the solubility of this salt is not sufficiently different from that of the target rhenium complex, and this precluded the isolation of **2** as a pure sample. Based on these results, we decided to use acetylides as nucleophiles because (a) they do not have hydrogens that could be transferred to the imido-N atom and (b) they can be easily obtained as a non-lithium alkaline salts.

The reaction of K[C≡CPh] (prepared by a reaction between phenylacetylene and K[N(SiMe$_3$)$_2$]) with benzonitrile and subsequent addition of the mixture to a solution of [Re(OTf)(CO)$_3$(bpy)] afforded the complex [Re{N=C(Ph)C≡CPh}(CO)$_3$(bpy)] (**3**) (Fig. 2). The alkylideneamido nature of this compound was initially inferred from its spectroscopic data. As expected for the formation of an alkylideneamido ligand, which has a strong donor character, complex **3** displays very low ν_{CO} band values (1999, 1899 and 1883 cm^{-1}) in its IR spectrum, in good agreement with the values reported

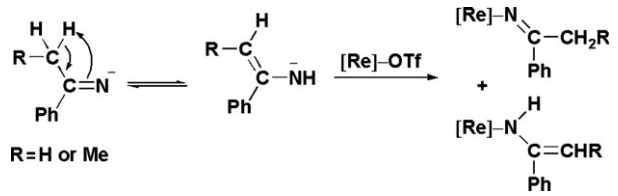


Scheme 1

[a] *Departamento de Química Orgánica e Inorgánica-IUQOEM, Facultad de Química, Universidad de Oviedo-CSIC, C/Julián Clavería no 8, Oviedo 33006, Spain. E-mail: japm@uniovi.es; Fax: +34 985103446; Tel: +34 985103465*
[b] *IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Valladolid 47005, Spain*

† Electronic supplementary information (ESI) available: Crystallographic data in CIF or other electronic format (CCDC 675894). See DOI: 10.1039/b801799a

‡ Current address: Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712-0165, USA.



Scheme 2

for complex **1** (1999, 1898 and 1880 cm^{-1}). Attempts to prepare **2** by the reaction of potassium phenylacetylide (prepared from $K[N(SiMe_3)_2]$ and phenylacetylene) with $[Re(NCPh)(CO)_3(bpy)]BAr'_4$[7] afforded a mixture of $[Re(CCPh)(CO)_3(bpy)]$[7] and **2**.

A single-crystal X-ray diffraction study confirmed the formation of an alkylideneamido complex.† A graphical representation of the results of the study is shown in Fig. 3.

The solid state structure of **3** consists of an otherwise unremarkable $[Re(CO)_3(bpy)]$ fragment bonded to the nitrogen atom of the alkylideneamido ligand, resulting from the coupling between the acetylide and the nitrile. The Re(1)–N(3)–C(4) angle (131.9(6)°) clearly indicates the absence of π-donation from the nitrogen to the metal (this kind of interaction would cause the formation of angles close to 180°, as it occurs in the azavinylidene complexes). The Re–N–C angle in **3** is in fact actually slightly lower that the same angle in complex **1** (133.9(4)°).[2] The Re–N distance in **3** is 2.130(6) Å, similar to the distance found in complex **1** (2.113(4) Å). When compared with rhenium azavinylidene complexes (for example $[Re(OH)(NC{=}Me_2)(Ph_2PCH_2CH_2PPh_2)_2][HSO_4]$ (1.901(5) Å) and $[ReCl\{NC{=}(H)(4\text{-}FC_6H_4)\}(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$ (1.831(8) Å)),[8] these values also reflect the lack of multiple-bond character of the Re–N bond in complex **3**.

In summary, we have successfully developed a new approach for the preparation of alkylideneamido complexes based on the *in situ*-generation of alkaline imidates by the reaction of appropriate carbanionic reagents and nitriles.

We thank the Ministerio de Ciencia y Tecnología (grants BQU2003-08649 and CTQ2006-07036), the Ministerio de Educación y Ciencia (grant CTQ-2006-08924, an FPU predoctoral fellowship to L. C. and a Ramón y Cajal contract to D. Morales) and Junta de Castilla y León (grant VA012C05) for their support of this work.

Experimental

General considerations

All experiments were carried out under a dinitrogen atmosphere employing Schlenk techniques. The solvents were

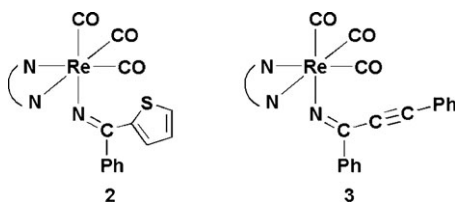


Fig. 2 Alkylideneamido complexes **2** and **3**.

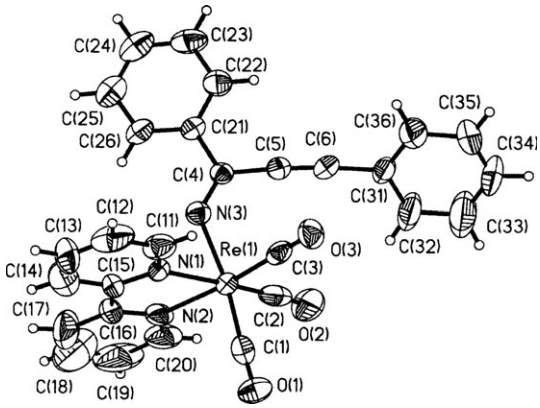


Fig. 3 Thermal ellipsoid (30%) plot of **3**.

freshly distilled prior to use. CH_2Cl_2 was dried over CaH_2, THF and diethyl ether were dried over Na-benzophenone, and hexane was dried over sodium. Benzonitrile was dried with $CaCl_2$ prior to distillation over P_2O_5. $K[N(SiMe_3)_2]$ (0.5 M in toluene, Aldrich), 2-thienyllithium (1.0 M in THF, Aldrich) and phenylacetylene (Aldrich) were used as supplied. $[Re(OTf)(CO)_3(bpy)]$ was prepared according to a literature procedure.[9] ^1H NMR spectra were recorded in CD_2Cl_2 (stored in the dark under a dinitrogen atmosphere over molecular sieves) on a Bruker AV-400 spectrometer. IR spectra were recorded in a Perkin-Elmer RX I FT-IR spectrometer using 0.2 mm CaF_2 cells. Elemental analyses were carried out using a Fisons EA-1108 analyzer (C, H and N) at the analytical services section of the Universidad de Vigo (Vigo, Spain).

Synthesis of 2

2-Thienyllithium (170 μL, 0.17 mmol, 1.0 M in THF) was added to a solution of benzonitrile (1 mL) in THF (10 mL) at −78 °C and stirred at room temperature for 15 min. The resulting solution was transferred to a solution of $[Re(OTf)(CO)_3(bpy)]$ (0.100 g, 0.17 mmol) in THF (10 mL) at −78 °C. After reaching room temperature, the solvent was evaporated under reduced pressure to a volume of 5 mL. The addition of hexane (20 mL) caused the precipitation of a red-orange solid, which was washed with diethyl ether (2 × 5 mL) and dried under vacuum. IR (THF; cm^{-1}): ν_{CO} = 1999, 1898 and 1882. ^1H NMR (CD_2Cl_2; ppm): 8.84 [d, J = 5.5 Hz, 2H, bpy], 8.27 [m, 2H, bpy], 8.08 [m, 2H, bpy], 7.41 [m, 2H, bpy], 7.34–7.32 [m, 4H], 7.19–7.14 [m, 2H], 6.93 [m, 1H] and 6.76 [m, 1H]. No satisfactory elemental analysis could be obtained.

Synthesis of 3

$K[N(SiMe_3)_2]$ (0.35 mL, 0.17 mmol, 0.5 M in toluene) was slowly added to a solution of phenylacetylene (22 μL, 0.17 mmol) in THF (10 mL) at −78 °C. Benzonitrile (70 μL, 0.68 mmol) was added to the resulting suspension, and the reaction mixture was stirred for 6 h at room temperature. At this point, a solution of $[Re(OTf)(CO)_3(bpy)]$ (0.100 g, 0.17 mmol) in THF (10 mL) was transferred into the reaction mixture at −78 °C. The resulting solution displayed a dark red color. After reaching room temperature, allowing 15 min for stirring, evaporating the solvent, extracting with CH_2Cl_2 (2 × 10 mL), concentrating, precipitating by the addition of diethyl ether

(15 mL) and washing with more of the same solvent (2 × 10 mL), compound **3** was obtained as a microcrystalline solid. Crystallization from THF–hexane yielded **3** as dark red crystals. Yield: 0.068 g (63%). IR (THF; cm^{-1}): ν_{CO} = 1999, 1899 and 1883. ^1H NMR (CD_2Cl_2; ppm): 9.23 [m, 2H, bpy], 8.86 [m, 2H, bpy], 8.32–8.04 [m, 8H, Ph] and 7.58–7.14 [m, 6H, bpy and Ph]. This compound decomposed during ^{13}C NMR studies. Anal. calc. for $C_{28}H_{18}N_3O_3Re$: C, 53.24; H, 2.87; N, 6.66. Found: C, 53.31; H, 2.67; N, 6.88%.

X-Ray diffraction study of 3

Data were collected using a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo-K_α X-radiation and a CCD area detector. Raw frame data were integrated using the SAINT[10] program. A semi-empirical absorption correction was applied by the program SADABS.[11] The structure was solved by direct methods and refined against $F2$ using SHELXTL.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. Crystal data for **3**: $C_{28}H_{18}N_3O_3Re$, M = 630.65, red plate (0.23 × 0.14 × 0.08 mm), monoclinic, $P2_1/n$, a = 11.039(7), b = 11.132(7), c = 20.67(1) Å, β = 102.73(1)°, V = 2478(3) $Å^3$, Z = 4, D_{calc} = 1.62 g cm^{-3}, μ(Mo-K_α) = 4.938 mm^{-1}, 3586 independent reflections, 2429 observed ($I > 2\sigma(I)$), R_{int} = 0.0481, $R1$ = 0.0401, w$R2$ = 0.0836 (all data).†

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