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Different sites of insertion in the reaction of isocyanates with [Re(N(R)Ar)(CO)$_3$(bipy)] (R = H or Me): N–H *vs.* Re–N†

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Received (in Cambridge, UK) 11th April 2002, Accepted 5th July 2002
First published as an Advance Article on the web 17th July 2002

The reactions of isocyanates with [Re(N(R)Ar)(CO)$_3$(bipy)] complexes lead to R′NCO insertion into the Re–N bond (for R = Me) or the N–H bond (R = H)

The amido ligand in complexes with a high electron count[1] is strongly nucleophilic due to π conflict with filled metal d orbitals.[2] As a result, activated substrates such as CO_2, CS_2, isocyanates,[3] *etc*., react with neutral saturated amido complexes, current mechanistic views favoring direct (without dissociation to give free amide ion), intermolecular (without previous substrate coordination) attack by the amido ligand to the electrophilic carbon. Most of these investigations have been carried out with groups 8–10 complexes.[4] Rhenium(I) amido complexes are known;[5] however, their insertion reactivity seems to be limited to a single report.[6] We recently prepared the 18 electron [Re(N(R)Ar)(CO)$_3$(bipy)] (R = H or aryl; bipy = 2,2′-bipyridine) complexes.[7] The lack of ligands either bulky or labile in these species should simplify the study of their reactivity.

The amido complex [Re(NH*p*-Tol)(CO)$_3$(bipy)] (**1**) reacted with EtNCO and with ^{t}BuNCO to afford [Re{N(*p*-Tol)C(O)NHEt}(CO)$_3$(bipy)] (**4a**)[8] and [Re{N(*p*-Tol)C(O)NH^{t}Bu}(CO)$_3$(bipy)] (**4b**),[9] respectively. These products were spectroscopically characterized and, for **4a**, also by X-ray diffraction (Fig. 1). †‡**4a** is the product of the formal isocyanate insertion into the N–H bond of **1** (as depicted in Scheme 1).

This type of insertion was previously found in the reactions of isocyanates with some free amines[10] and amido complexes.[11] For the latter, direct amido attack to the isocyanate, resulting in RNCO insertion into the M–N bond has been proposed as a first step on the basis of the NMR spectra of ^{15}N-labeled compounds.[12] A subsequent rearrangement involving H^+ transfer would afford the final observed product of formal insertion into the N–H bond. Unable to detect the intermediate obtained as the product of the first step, we reasoned that using an amido complex without N–H bonds would render it stable.

The diphenylamido complex [Re(NPh$_2$)(CO)$_3$(bipy)] (**2**)[7] did not react with RNCO (R = Et, ^{t}Bu, Ph) (refluxing toluene, 6 h),

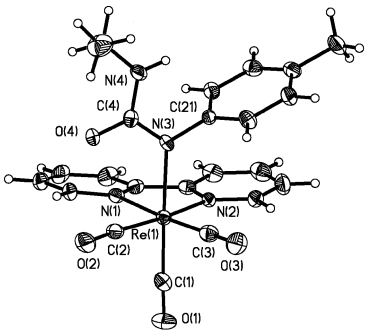
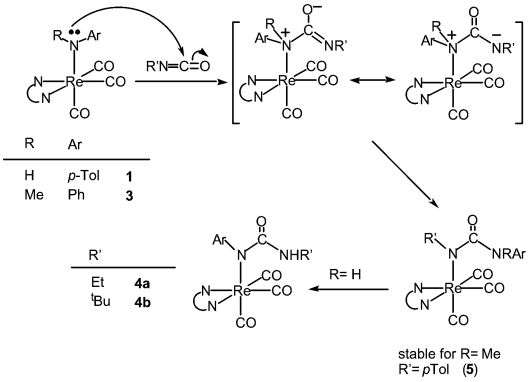


Fig. 1 Thermal ellipsoid (30%) plot of **4a**.

† Electronic supplementary information (ESI) available: experimental details for all the new compounds. See http://www.rsc.org/suppdata/cc/b2/b203261a/



Scheme 1

a fact attributed to insufficient nucleophilicity of **2**. Hence, we prepared (by reaction of KN(Me)Ph with [Re(OTf)(CO)$_3$(bipy)])[13] the new compound [Re(N(Me)Ph)(CO)$_3$(bipy)](**3**),[14] which was spectroscopically characterized. Its IR spectrum, showing ν_{CO} values similar to those of **1**, seemed to us encouraging regarding a comparable nucleophilicity. Indeed, **3** reacted with *p*-TolNCO to afford **5**,[15] the product of isocyanate insertion into the Re–N bond, which was characterized both spectroscopically and by X-ray diffraction (Fig. 2).†‡

These findings are summarized in Scheme 1, in which the bracketed zwitterionic species is the transition state or intermediate obtained by attack of the amido complex on the isocyanate. The amine end of the resulting ligand would be displaced by the amido end, a better donor, to afford the product of formal insertion into the Re–N bond. For R = Me this species is stable, and is the observed product. However, for R = H, H and {Re(CO)$_3$(bipy)} exchange nitrogen sites. For R′ = Et and ^{t}Bu this last equilibrium is completely displaced towards the N–H inserted product (compounds **4a** and **4b**). The driving force for the H/Re exchange can be traced to the higher acidity of the NHAr group compared with NHEt or NH^{t}Bu; proto-

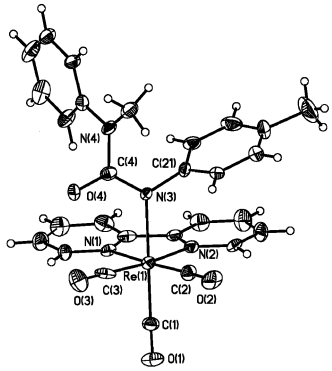
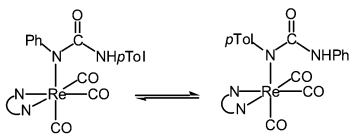


Fig. 2 Thermal ellipsoid (30%) plot of **5**.

DOI: 10.1039/b203261a



Scheme 2

nolysis of the Re–NR′ bond by the –NHAr acid would generate a –NAr amido group, which displaces a –NHR′ amino group from the rhenium center. In contrast, the reaction of **1** with PhNCO afforded a mixture of two products. This is consistent with the mechanism proposed above: now, the acidity of the –NHPh and –NH*p*-Tol groups is comparable, and there is an equilibrium between the product of formal insertion into the N–H and Re–N bonds, as shown in Scheme 2.

The reaction of **1** with PhNCO is instantaneous, while **1** takes 10–20 min to react with EtNCO and ^{t}BuNCO. This can be attributed to the higher electrophilic character of the aryl isocyanate. Complex **3** reacts with *p*-TolNCO (15 min), but does not with EtNCO or ^{t}BuNCO, indicating that the steric hindrance of the amido nitrogen substituents is important. None of the insertion products mentioned above reacts further with isocyanates. The structures of **4a** and **5** show that this can be attributed to the delocalization of the amido lone pair. This delocalization involves mainly the carbonyl groups of the N(Ar)C(O)NRR′ ligands: the N(3)–C(4) distances are 1.362(7) (**4a**) and 1.344(13) Å (**5**), respectively, consistent with some degree of multiplicity, whereas the N(3)–C(21) distances [1.445(7) (**4a**) and 1.427(13) Å (**5**)] are significantly longer than in amido complexes (1.360(5) Å for the complex [Re(NHPh)(CO)$_3$(bipy)]).[7]

In summary, the studies reported here strongly support that the reaction of amido complexes with isocyanates proceeds *via* initial nucleophilic attack of the amido ligand, followed by an exchange of the metal-bound nitrogen group. The resulting product may be stable or undergo H^+ transfer-assisted exchange of the M-bound nitrogen.

We thank Ministerio de Ciencia y Tecnología and Ministerio de Educación, Cultura y Deporte for support of this work (Projects MCT-00-BQU-0220, PB97-0470-C02-01 and PR-01-GE-7) and a predoctoral fellowship (to E. H.).

Notes and references

‡ *Crystal data* for **4a**: $C_{23}H_{21}ClN_4O_4Re{\cdot}0.5CH_2Cl_2$, M = 646.10, monoclinic, space group $P2_1/c$, a = 17.650(2), b = 8.5444(11), c = 16.448(2) Å, α = 90, β = 105.882(2), γ = 90°, V = 2385.8(5) Å^3, T = 293 K, Z = 4, D_{calc} = 1.799 Mg m^{-3}, F(000) = 1260, μ(Mo-Kα) = 5.243 mm^{-1}, reflections collected/unique = 10333/3444 (R_{int} = 0.0332), parameters: 309, final R_1 = 0.0356, wR_2 = 0.0606 (all data), GoF = 1.005, max/min residual electron density 1.058/−1.067 e Å^{-3}. *Crystal data* for **5**: $C_{28}H_{23}N_4O_4Re$, M = 665.70, monoclinic, space group $P2_1/n$, a = 10.056(2), b = 25.335(6), c = 10.233(2) Å, α = 90, β = 98.774(4), γ = 90°, V = 2576.7(10) Å^3, T = 293 K, Z = 4, $D_{calc.}$ = 1.716 Mg m^{-3}, F(000) = 1304, μ(Mo-Kα) = 4.757 mm^{-1}, reflections collected/unique = 11333/3699 (R_{int} = 0.0655), parameters: 336, final R_1 = 0.0547, wR_2 = 0.1293 (all data), GoF = 1.031, max/min residual electron density 3.165/−1.486 e Å^{-3}, solution and refinement using SHELXL.[16] CCDC reference numbers 182882 and 182883. See http://www.rsc.org/suppdata/cc/b2/b203261a/ for crystallographic data in CIF or other electronic format.

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8 **Reaction of 1 with EtNCO.** EtNCO (6.6 µL, 0.109 mmol) was added to a solution of **1** (0.050 g, 0.086 mmol) in THF (15 mL). The color of the solution changed from green to red. The solvent was removed under vacuum and the red solid was redisolved in CH_2Cl_2 (5 mL). Slow diffusion of hexanes into this solution at room temperature afforded red crystals, one of which was employed for an X-ray structure determination. Yield: 95% (0.046 g). Anal. Calc. for $C_{23}H_{21}N_4O_4Re$: C, 45.76; H, 3.50; N, 9.28. Found: C, 45.68; H, 3.46; N, 9.19%. IR (THF): 2014, 1913, 1886. ^{1}H NMR (CD_2Cl_2): 8.78, 8.07, 7.92, 7.24 [m, 2H each, bipy], 6.68, 6.65, 6.17, 6.14 [AA′BB′, 4H, *p*-Tol], 3.34 [s, broad, 1H, N*H*], 2.83 [q (7.1), 2H, NCH_2CH$_3$], 2.07 [s, 3H, CH$_3$, *p*-Tol], 0.70 [t (7.1), 3H, NCH$_2$CH_3]. ^{13}C{^{1}H} NMR(CD_2Cl_2): 199.66 [2CO], 193.82 [CO], 162.63 [O=C], 155.70, 154.67 [bipy], 148.70 [*p*-Tol], 138.76 [bipy],132.73, 129.51, 128.15 [*p*-Tol], 126.42, 122.58 [bipy], 36.39 [N*C*H$_2$CH$_3$], 20.79 [CH$_3$, *p*-Tol], 15.91 [NCH_2*C*H$_3$].

9 **Reaction of 1 with ^{t}BuNCO.** ^{t}BuNCO (9.5 µL, 0.083 mmol) was added to a solution of **1** (0.050 g, 0.083 mmol) in THF (15 mL). Subsequent workup as described for **4a** afforded red crystals of **4b**. Yield: 92% (0.048 g). Anal. Calc. for $C_{25}H_{25}N_4O_4Re$: C, 47.53; H, 3.98; N, 8.86. Found: C, 47.57; H, 3.95; N, 8.89%. IR (THF): 2014, 1913, 1887. ^{1}H NMR (CD_2Cl_2): 8.81, 8.09, 7.91, 7.23 [m, 2H each, bipy], 6.67, 6.63, 6.17, 6.13 [AA′BB′, 4H, *p*-Tol], 3.40 [s, broad, 1H, N*H*], 2.14 [s, 3H, CH$_3$, *p*-Tol], 0.92 [s, 9H, NC(CH_3)]. ^{3}C{^{1}H} NMR (CDCl): 199.72 [2CO], 193.89 [CO], 161.93 [O=C], 155.65, 154.88 [bipy], 149.29 [*p*-Tol], 138.62 [bipy], 132.28 [*p*-Tol], 129.45 127.97 [*p*-Tol], 126.12, 122.37 [bipy], 49.86 [N*C*(CH$_3$)], 29.55 [NC(*C*H$_3$)$_3$], 20.72 [CH$_3$, *p*-Tol].

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14 **Preparation of [Re(NMePh)(CO)$_3$(bipy)] (3).** A solution of KNMePh (0.094 mmol) in THF (5 mL) at −78 °C was added to a solution of [Re(OTf)(CO)$_3$(bipy)] (0.050 g, 0.086 mmol) in THF (15 mL) cooled to −78 °C. The mixture was allowed to reach room temperature. Volatiles were removed under vacuum, the green solid was extracted with CH_2Cl_2 (2 × 10 mL) and the solution was filtered using a cannula tipped with filter paper. Slow diffusion of hexanes into a solution of **3** in THF at −20 °C afforded a green microcrystalline solid. Yield: 0.036 g, 73%. Anal. Calc. for $C_{20}H_{16}N_3O_3Re$: C, 45.10; H, 3.02; N, 7.88. Found: C, 45.21; H, 3.10; N, 7.79%. IR (THF): 2006, 1896, 1877. ^{1}H NMR (CD_2Cl_2): 9.20 [m, 2H, bipy], 8.02 [m, 4H, bipy], 7.48 [m, 2H, bipy], 6.72 [m, 2H, Ph], 6.30 [m, 2H, Ph], 6.02 [m, 1H, Ph], 2.39 [s, 3H, NMe].

15 **Reaction of 3 with *p*-TolNCO.** *p*-TolNCO (10 µL, 0.083 mmol) was added to a solution of **3** (0.050 g, 0.083 mmol) in THF (15 mL). The mixture was stirred for 15 minutes and the color of the solution changed from green to orange. The solvent was removed under vacuum and the solid residue was redissolved in CH_2Cl_2 (5 mL). Slow diffusion of hexanes into this solution at −20 °C afforded orange crystals, one of which was used for an X-ray diffraction determination of the structure. Yield: 88% (0.048 g). Anal. Calc. for $C_{28}H_{25}N_4O_4Re$: C, 50.36; H, 3.77; N, 8.39. Found: C, 50.31; H, 3.75; N, 8.43%. IR (THF): 2014, 1913, 1888. ^{1}H NMR (CD_2Cl_2): 8.89, 8.04, 7.94, 7.26 [m, 2H each, bipy], 6.90 [m, 3H, Ph], 6.63 [m, 2H, Ph] 6.44, 6.40, 6.29, 6.25 [AA′BB′, 4H, *p*-Tol], 2.59 [s, 3H, NCH_3], 2.02 [s, 3H, CH$_3$, *p*-Tol]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 199.17 [2CO], 193.82 [CO], 166.10 [O=C], 155.73, 155.14 [bipy], 148.72, 148.14 [*p*-Tol, Ph], 138.91 [bipy], 131.35, 128.59, 128.34 [*p*-Tol, Ph], 126.77, 126.36 [bipy, *p*-Tol], 122.49 [bipy], 121.17, 119.17 [Ph], 37.69 [NCH$_3$], 20.63 [CH$_3$, *p*-Tol].

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