Inorg. Chem. **2002**, *41*, 4111–4113

Formation of a 1-Azaallenylidene Ligand by Reaction of an Amido Complex with Tetracyanoethylene

Dolores Morales,[†] Julio Pérez,*[,†] Lucía Riera,[†] Víctor Riera,[†] and Daniel Miguel[‡]

Departamento de Química Orgánica e Inorgánica/IUQOEM Facultad de Química, Universidad de Oviedo-CSIC, 33071, Oviedo, Spain, and Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 44071 Valladolid, Spain

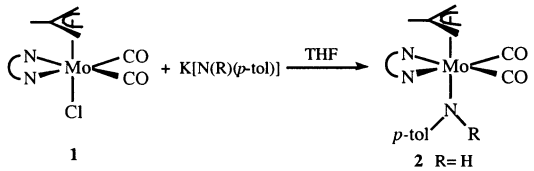
Received April 23, 2002

Amido complexes of Mo(II) allyl carbonyl fragments containing monodentate amido ligands, prepared by reaction of suitable chloro precursors with potassium amides, react (for the N(H)(*p*-tolyl) derivative) with tetracyanoethylene to give a 1-azaallenylidene complex.

The strong electrophile tetracyanoethylene (TCNE) reacts with organic amines undergoing the sequential replacement of two CN groups to afford 1,1-diamino-2,2-dicyanoethylenes.[1] The reactivity of TCNE toward N-metalated amines, i.e., amido complexes, has not been studied. Coordination compounds containing polycyanoethylene moieties, which could be envisaged as products, have attracted considerable attention.[2] Amido complexes may show an enhanced reactivity compared with free amines as a result of π conflict between the nitrogen lone pair of the amido ligand and filled metal d orbitals.[3] However, in most stable amido compounds, this reactivity is mitigated by π donation from the amido nitrogen to empty d orbitals, by steric hindrance due to bulky ancillary ligands, or by both factors.[4]

We recently found that the reaction of [MoCl(η^3-allyl)(CO)$_2$(phen)] (phen = 1,10-phenanthroline) complexes with NaOMe affords stable yet highly reactive alkoxo complexes,[5] and we thought that a similar route could be used to prepare amido derivatives. Here we report the synthesis and structure of new amido complexes [Mo(N(*p*-tolyl)R)(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (R= H or *p*-tolyl) and their reactivity toward TCNE.

Scheme 1



The reactions of [MoCl(η^3-C$_3$H$_4$-Me-2)(CO)$_2$(phen)] (**1**) with K[NR(*p*-tol)] (R = H or *p*-tolyl) afforded the amido complexes [Mo(N(*p*-tol)R)(η^3-C$_3$H$_4$Me-2)(CO)$_2$(phen)][6] (R = H, **2**; *p*-tolyl, **3**) (Scheme 1), which were characterized by IR and NMR spectroscopy and, for **3**, by X-ray diffraction (Figure 1).[7]

* Author to whom correspondence should be addressed. E-mail: japm@sauron.quimica.uniovi.es. Fax: 0034985103446.

† Universidad de Oviedo-CSIC.

‡ Universidad de Valladolid.

(1) (a) Fatiadi, A. J. *Synthesis* **1986**, 249. (b) Dhar, D. N. *Chem. Rev.* **1967**, *67*, 611. (c) Cairns, T. L.; McKusick, B. C. *Angew. Chem.* **1961**, *73*, 520.

(2) (a) Hartmann, H.; Kaim, W.; Hartenbach, I.; Schleid, T.; Wanner, M.; Fiedler, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2842. (b) Nemykin, V. N.; Kobayashi, N. *Chem. Commun.* **2001**, 165. (c) Gordon, D. C.; Deakin, L.; Arif, A. M.; Miller, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 290. (d) Pokhodnya, K. I.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* **2000**, *12*, 410. (e) Hoshino, H.; Iida, K.; Kawamoto, T.; Mori, T. *Inorg. Chem.* **1999**, *38*, 4229.

(3) (a) Jayaprakash, K. N.; Gillepsie, A. M.; Gunnoe, T. B.; White, D. P. *Chem. Commun.* **2002**, 372. (b) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25. (c) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125.

(4) (a) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623. (b) Jayaprakash, K. N.; Conner, D.; Gunnoe, T. B. *Organometallics* **2001**, *20*, 5254. (c) Flood, T. C.; Lim, J. K.; Deming, M. A.; Keung, W. *Organometallics* **2000**, *19*, 1166. (d) Cummins, C. C. *Chem. Commun.* **1998**, 1777. (e) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6916. (f) Francisco, L. W.; White, P. S.; Templeton, J. L. *Organometallics* **1996**, *15*, 5127.

(5) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1750.

(6) Synthesis of **2**: K[N(H)(*p*-tol)] (0.26 mmol) in THF (10 mL) was added to a solution of **1** (100 mg, 0.24 mmol) in THF (10 mL) at −78 °C. After stirring for 10 min, in vacuo solvent evaporation, extraction of the residue (CH_2Cl_2, 2 × 5 mL), filtration (Celite), in vacuo concentration to 5 mL, layering with hexane (20 mL), and standing at −20 °C, red crystals were obtained. Yield: 107 mg, 92%. Anal. Calcd for $C_{25}H_{23}MoN_3O_2$: C, 60.86; H, 4.70; N, 8.52. Found: C, 60.71; H, 4.97; N, 8.55. IR (ν_{CO}) (CH_2Cl_2): 1926, 1839. ^{1}H NMR (CD_2Cl_2): 8.94 [dd ($J_{H2,3} = J_{H9,8} = 5.0$, $J_{H2,4} = J_{H7,9} = 1.3$), 2H, $H_{2,9}$], 8.45 [dd ($J_{H4,3} = J_{H7,8} = 8.6$ Hz), 2H, $H_{4,7}$], 7.99 [s, 2H, $H_{5,6}$], 7.76 [dd, 2H, $H_{3,8}$], 6.69, 6.66, 6.60 and 6.57 [AA′BB′, 4H, C_6H_4], 3.90 [s br, 1H, N−*H*], 3.00 [s, 2H, H_s], 2.08 [s, 3H, C_6H_4−C*H*$_3$], 1.48 [s, 2H, H_a], 0.64 [s, 3H, η^3-C$_3$H$_4$(C*H*$_3$)-2]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 231.4 [CO], 158.8, 151.7, 144.5, 137.4, 130.6, 129.4, 127.7, 125.3, 121.7 and 115.8 [phen and C_6H_4], 87.8 [C^2, η^3-C$_3$H$_4$(CH$_3$)], 68.1 [C^1 and C^3, η^3-C$_3$H$_4$(CH$_3$)-2], 26.0 [C_6H_4−*C*H$_3$], 20.1 [η^3-C$_3$H$_4$-(*C*H$_3$)-2].

(7) Crystal data for **3**: $C_{32}H_{29}MoN_3O_2$, M = 583.52, monoclinic, space group $P2_1/n$, a = 13.194(4) Å, b = 12.113(3) Å, c = 17.992(5) Å, β = 105.471(4)°, V = 2771.1(13) Å^3, T = 293 K, Z = 4, D_{calcd} = 1.399 Mg/m^3, $F(000)$ = 1200, μ(Mo Kα) = 0.507 mm^{-1}, reflections collected/unique = 11944/3978 (R_{int} = 0.0828); parameters, 346; final R1 = 0.0789, wR2 = 0.1178 (all data), GOF= 1.010, max/min residual electron density 0.698/−0.715 e Å^{-3}, solution and refinement using SHELXL.[20]

10.1021/ic025665b CCC: $22.00
Published on Web 07/13/2002

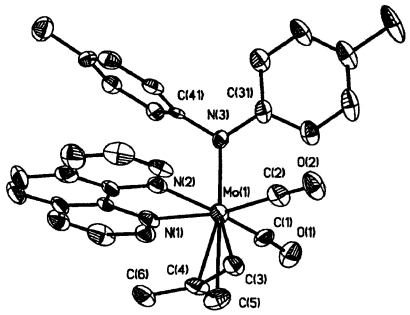


Figure 1. Molecular structure and numbering scheme of **3** with hydrogen atoms omitted for clarity.

As in previous reactions of chloro complexes such as **1** with carbanions[8] and alkoxides,[5] the amide anion gives the stereospecific Cl^- substitution, in contrast with the well-known allylic alkylation observed with malonate or other resonance stabilized anions.[9] Thus, in the molecule of the product, the allyl and amido groups are on opposite sides of the plane defined by the phen nitrogens and the two carbonyls.

The ν_{CO} IR bands of **2** and **3** are even lower than those of related alkoxo derivatives,[5] reflecting the strongly donating properties of the amido groups.

The ^{1}H NMR spectra of **2** between 25 and −80 °C include a set of four phen signals, consistent either with free rotation around the Mo−N bond or with a single rotamer possessing a mirror plane. Since in the solid state structure of **3** (Figure 1) the two *p*-tolyl groups are inequivalent, but only one set of *p*-tolyl signals is seen in the ^{1}H NMR between 25 and −80 °C, free rotation around the Mo−N seems more plausible. On the other hand, free rotation can be expected for complexes that, like **2** and **3**, are electron precise considering single Mo−N(amido) bonds, and lack any steric hindrance.[10] The amido group of **3** is planar at nitrogen, a feature of most structurally characterized amido complexes.[11] For electron-precise compounds such as **2** and **3**, this fact is interpreted as due to electron delocalization involving the substituents of the amido ligand. In fact, lowering the temperature causes the broadening of the AA′BB′ signal of the *p*-tolyl groups of **2** and **3**, indicating that the rotation around the N−(*p*-tolyl) bonds is being frozen, in accord with delocalization of the lone pair on the amido nitrogen over the aryl groups.

The chemistry of Mo(II) carbonyl complexes has been extensively studied;[12] nevertheless, amido complexes of this type are rare. Lack of selectivity in the synthetic reactions and the CO-labilizing effect of the amido group[13] can explain this paucity of derivatives.[14]

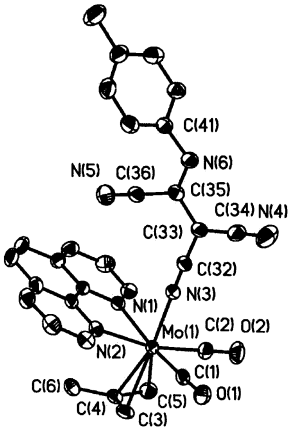
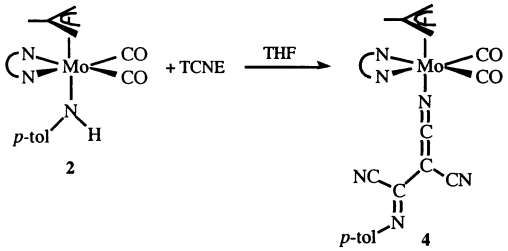


Figure 2. Molecular structure and numbering scheme of **4** with hydrogen atoms omitted for clarity.

Scheme 2



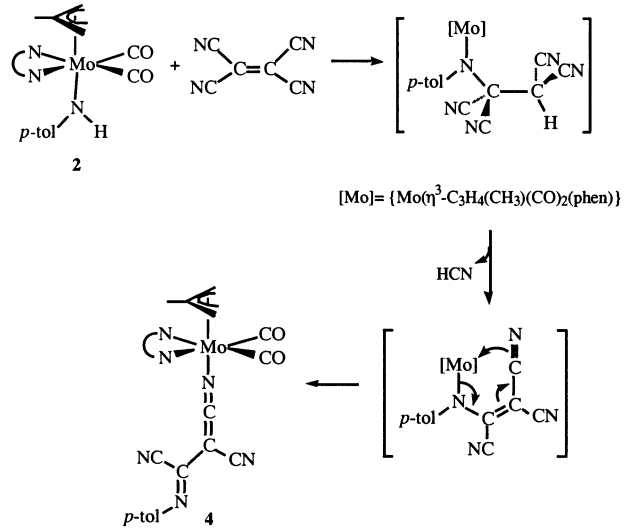
Strong electrophiles attack selectively the amido ligand of **2**. Thus, reactions with HOTf and MeI afforded [Mo(η^3-C_3H_4-Me-2)(NH_2(*p*-tol))$(CO)_2$(phen)]OTf and [MoI(η^3-C_3H_4-Me-2)$(CO)_2$(phen)], respectively. The better ligating properties of I^- compared with OTf^- explain the different types of products.

The tolylamido complex **2** reacts with TCNE to give [Mo{N═C═C(CN)C(CN)(C═N(*p*-tol))}(η^3-C_3H_4-Me-2)$(CO)_2$(phen)][15] (**4**) (Scheme 2), characterized by spectroscopy and X-ray diffraction (Figure 2).[16]

In **4** a {Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)} fragment (whose geometry is like that of the precursor **2**) is bound to a

(8) Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E. *J. Am. Chem. Soc.* **2001**, *123*, 7469.
(9) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543.
(10) A similar behavior has been recently found for amido complexes [Re(NRR′)$(CO)_3$(N-N)]; see: Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1966.
(11) The only exceptions: (a) Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1991**, 712. (b) Dewey, M. A.; Stark, G. A.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4798. (c) Jayaprakash, K. N.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2001**, *40*, 6481.
(12) Baker, P. K. *Adv. Organomet. Chem.* **1995**, *40*, 45.
(13) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 1535.
(14) Mo(II) or W(II) amido complexes: (a) Caldarelli, J. L.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10097. (b) Powell, K. R.; Pérez, P. J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851. Considering single M−N bonds; i.e., not counting π donation from N to M, these are 16 electron compounds. Using the same counting scheme, the amido complexes reported in the present paper are 18 electron species.
(15) Synthesis of **4**: TCNE (16 mg, 0.12 mmol) was added to **2** (50 mg, 0.10 mmol) in THF (20 mL). **CAUTION!** *The HCN byproduct is extremely toxic!* Workup as for **2** gave red crystals. Yield: 56 mg, 94%. Anal. Calcd for $C_{30}H_{22}MoN_6O_2$: C, 60.61; H, 3.73; N, 14.14. Found: C, 60.32; H, 4.01; N, 14.37. IR (CH_2Cl_2): 2206 ($\nu_{C\equiv N}$), 2167 ($\nu_{C=N}$), 1961, 1881 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 9.17 [dd ($J_{H2,3} = J_{H9,8} = 5.0$, $J_{H2,4} = J_{H7,9} = 1.3$), 2H, $H_{2,9}$], 8.48 [dd ($J_{H4,3} = J_{H7,8} = 8.1$), 2H, $H_{4,7}$], 7.89 [s, 2H, $H_{5,6}$], 7.02 [dd, 2H, $H_{3,8}$], 6.48 [s broad, 4H, C_6H_4], 3.26 [s, 2H, H_s], 2.30 [s, 3H, C_6H_4−CH_3], 1.70 [s, 2H, H_a], 0.70 [s, 3H, η^3-C_3H_4(CH_3)-2]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 224.2 [CO], 152.2, 148.7, 145.2, 139.1, 134.2, 131.0, 129.4, 127.9, 125.5 and 120.9 [phen and C_6H_4], 85.5 [C^2, η^3-$C_3H_4(CH_3)$], 56.8 [C^1 and C^3, η^3-C_3H_4-(CH_3)-2], 21.0 [C_6H_4−CH_3], 18.8 [η^3-C_3H_4(CH_3)-2].
(16) Crystal data for **4**: $C_{31}H_{24}Cl_2MoN_6O_2$, $M = 679.40$, monoclinic, space group $P2_1/n$, $a = 8.602(3)$ Å, $b = 17.697(5)$ Å, $c = 20.147(6)$ Å, $\beta = 90.000(6)°$, $V = 3066.8(16)$ Å^3, $T = 293$ K, $Z = 4$, $D_{calcd} = 1.471$ Mg/m^3, $F(000) = 1376$, μ(Mo Kα) = 0.640 mm^{-1}, reflections collected/unique = 13599/4475 ($R_{int} = 0.0279$); parameters, 382; final R1 = 0.0491, wR2 = 0.1125 (all data), GOF = 1.038, max/min residual electron density 1.175/−0.862 e Å^{-3}, solution and refinement using SHELXL.[20]

Scheme 3



ketenimínato (1-azaallenylidene) ligand trans to the allyl group.

The formation of this ligand can be rationalized considering TCNE insertion into the N−H bond[17] of **2**, giving a tricyanovinylamine group, followed by 1,2-elimination of HCN[1] and intramolecular metal shift (Scheme 3).

The Mo−N−C−C grouping is linear (N(3)−C(32)−C(33) = 178.5(5)°, Mo(1)−N(3)−C(32) = 178.8(4)°). This can be explained assuming some multiple character for the bonds involved. The angles about C(33)[18] and C(35)[18] are close to 120°, suggesting sp^2 character of these carbons.

Although some complexes with related keteniminato ligands are known,[19] their preparation from amido complexes is unprecedented. The reactivity of **2** and **3** toward different electrophiles is under investigation.

Acknowledgment. We thank Prof. Agustín Galindo for insight, and Ministerio de Ciencia y Tecnología (Projects MCT-00-BQU2000-0220, PB97-0470-C02-01) and FICYT (PR-01-GE-7) for support and for predoctoral (L.R.) and postdoctoral (D.M.) fellowships.

Supporting Information Available: Crystal data for **3** and **4** and experimental details for all of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025665B

(17) Insertion of unsaturated electrophiles into N−H bonds of amido complexes: (a) Glueck, D. S.; Winslow, L. J. N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. (b) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319.

(18) C(32)−C(33)−C(34) = 118.7(4)°, C(32)−C(33)−C(35) = 120.7(4)°, C(34)−C(33)−C(35) = 120.6(4)°; C(33)−C(35)−C(36) = 115.2(4)°, N(6)−C(35)−C(36) = 121.8(4)°, N(6)−C(35)−C(33) = 123.0(4)°.

(19) (a) Bruce, M. I.; Wallis, R. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 2205. (b) Ricci, J. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2391. (c) Sacher, W.; Nagel, U.; Beck, W. *Chem. Ber.* **1987**, *120*, 895. (d) Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 8799.

(20) Sheldrick, G. M. *SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data*, version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.