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Reactivity of [MoX(η^3-allyl)(CO)$_2$(N−N)] Complexes with Simple, Nonstabilized Carbanions

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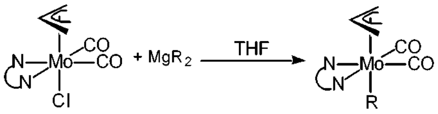
In 1982 Trost reported that [MoCl(η^3-allyl)(CO)$_2$(L−L)] (L−L = bidentate chelating ligand) complexes react with stabilized carbanions to yield olefins.[1] It remains unknown whether the nucleophilic attack takes place (a) directly to the allyl ligand or (b) to the metal, followed by a metal-to-allyl migration. In general, the site of primary nucleophilic attack in the reactions of η^3-allylmetal complexes is dictated by the nature of the nucleophile: hard nucleophiles prefer the metal, whereas soft, stabilized ones attack the allyl group.[2]

Pseudooctahedral [MoCl(η^3-allyl)(CO)$_2$(L−L)] complexes have been known for more than three decades.[3] However, their reactivity toward simple, nonstabilized carbanions remains so far unexplored.[4] We have initiated the study of this reactivity and here we report our preliminary results.

The orange complex [MoCl(η^3-allyl)(CO)$_2$(bipy)] (bipy = 2,2′-bipyridine) (**1a**)[3a−c] reacts in THF solution with methylating carbanionic reagents (vide infra) to give a single blue product **2a** with two C−O stretching bands of similar intensity in the IR spectrum, diagnostic of a *cis*-M(CO)$_2$ unit, at frequencies lower than the starting chlorocomplex. The ^{1}H NMR shows the three-signal pattern of a static, symmetrical, untouched η^3-allyl ligand, and a low-frequency singlet typical of a metal-bound methyl group. The pattern of four multiplets for the bipy hydrogens, maintained at low temperature (180 K), reveals the existence of a mirror plane in the molecule. Hence, [Mo(CH$_3$)(η^3-allyl)(CO)$_2$(bipy)](**2a**) has the geometry shown in Scheme 1, with the methyl and allyl groups in mutually trans positions.

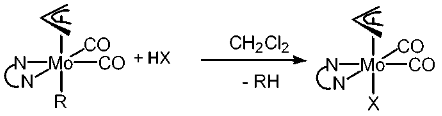
Scheme 1



	N-N
1a	bipy
1b	phen

	N-N	R	Yield (%)
2a	bipy	CH_3	57
2b	bipy	CH_2CH_3	52
2c	bipy	$CH_2C_6H_5$	79
3a	phen	CH_3	66
3b	phen	CH_2CH_3	58
3c	phen	$CH_2C_6H_5$	84

Scheme 2



X= OTf, SPh

When methyllithium was used as alkylating reagent, traces of other unidentified species were obtained together with **2a**; thus, more selective reagents were sought. Methylmagnesium iodide afforded spectroscopically pure **2a**; however, it transformed into a second, orange complex upon standing in solution at room temperature or during attempted isolation. The same result was found using lithium dimethylcuprate, prepared in situ by reaction of CuI and MeLi,[5] as carbanion source. The orange complex was found to be [MoI(η^3-allyl)(CO)$_2$(bipy)].[6] Dimethylmagnesium, selective and halide-free,[7] was found to be the reagent of choice. Slow formation of the chlorocomplex **1a** was observed in dichloromethane solutions of **2a**; thus, non-chlorinated solvents had to be used for workup and NMR studies.

To test the generality of our synthetic procedure and the stability of the alkyls, we prepared similarly the ethyl **2b** and benzyl **2c** derivatives, as well as the three analogues with N−N = 1,10-phenanthroline (phen) (compounds **3a**−**c**).[9] The alkylations were specific, and neither allylic alkylation nor acyl products were formed. The same result was found using [MoBr(η^3-allyl)(CO)$_2$(N−N)] complexes as starting materials.

The higher solubility of the complexes with the phen ligand allowed their ^{13}C NMR spectra to be acquired. The spectral data

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(1) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543−5545. Trost found that the reaction can be made catalytic in metal: molybdenum carbonyl complexes catalyze the reaction of allylic acetates with stabilized carbanions, such as the one obtained by deprotonation of diethyl malonate. For studies of the influence of the ligands on this reaction, see: Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590−9600. Sjögren, M. P. T.; Frisell, H.; Akermark, B.; Norrby, P.-O.; Eriksson, L.; Vitagliano, A. *Organometallics* **1997**, *16*, 942−950. For the asymmetric version of this reaction, see: Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104−1105.

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(4) To our knowledge, the only such reaction reported is that of [MoX(η^3-C$_3$H$_5$)(CO)$_2$(DAB)] (X= Cl, Br; DAB= N, N′-dialkylethanediimine) with MeLi or MeMgI, which afforded unidentified decomposition products: Hsieh, A. T. T.; West, B. O. *J. Organomet. Chem.* **1976**, *112*, 285−296. The possibility of nucleophilic attack to the metal was suggested: Curtis, M. D.; Fotinos, N. A. *J. Organomet. Chem.* **1984**, *272*, 43−54. In the study of the Mo-catalyzed allylic alkylation, Trost found results suggesting attack to the metal by the less bulky malonate anions: Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1987**, *109*, 1469−1478. For another example of at-the-metal attack by a soft nucleophile, see: Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670−1672.

(5) Caldarelli, J. L.; Wagner, L. E.; White, P. S; Templeton, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2878−2888.

(6) See Supporting Information for details.

(7) Actually, the dimethylmagnesium we used, prepared from MeMgI and 1,4-dioxane (see ref 6), contains some halide. A method to prepare truly halide-free dimethylmagnesium is given in ref 8. However, the extremely hazardous nature of HgMe$_2$ deterred us from using it.

(8) Cotton, F. A.; Wiensinger, K. J. *Inorg. Chem.* **1990**, *29*, 2594−2599.

(9) **3a:** To a solution of **1b** (0.10 g, 0.24 mmol) in THF (20 mL) was added MgMe$_2$ (0.26 mmol, 0.9 mL of a 0.29 M solution in Et$_2$O). After the mixture was stirred for 15 min, the solvent was removed under vacuum. The residue was extracted with toluene (4 × 10 mL) and filtered through Celite to yield a blue solution. The solvent was then removed under vacuum to afford 0.063 g of **3a** as a blue solid. IR (CH$_2$Cl$_2$): 1922, 1830 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): 8.96, 8.42, 7.97, and 7.71 [m, 2H each, phen], 3.05 [m, 1H, CH η^3-C$_3$H$_5$], 2.77 [d (6.4), 2H, H$_{syn}$], 1.49 [d (9.3), 2H, H$_{anti}$], −0.69 [s, 3H Mo−CH$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 235.60 [CO], 151.69, 144.36, 136.02, 130.49, 127.45, and 124.29 [phen], 73.56 [C^2 η^3-C$_3$H$_5$], 51.82 [C^1 and C^3 η^3-C$_3$H$_5$], 12.51 [Mo−CH$_3$]. **3b:** A similar procedure using **1b** (0.10 g, 0.24 mmol) and MgEt$_2$ (1.13 mL of a 0.21 M solution in ether, 0.24 mmol) gave the ethyl complex **3b** (0.057 g) as a violet solid. IR (CH$_2$Cl$_2$): 1919, 1827 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): 1.52 [t (7.9), 3H, CH$_3$], −0.29 [q (7.8), 2H, CH$_2$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 30.67 [CH$_3$], 19.82 [CH$_2$]. **(3c).** From **1b** (0.10 g, 0.24 mmol) and MgBz$_2$ (0.70 mL of a 0.34 M solution in THF, 0.24 mmol) **3c** (0.95 g) was obtained as a dark blue solid. IR (CH$_2$Cl$_2$): 1925, 1827 (ν_{CO}). ^{1}H NMR (C$_6$D$_6$): 6.14 and 5.14 [m, C$_6$H$_5$], 3.00 [s, 2H, CH$_2$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 152.07, 151.62, 144.27, 135.59, 130.19, 127.30, 126.26, 124.27, 124.15, and 118.57 [m, C$_6$H$_5$ and phen], 36.65 [CH$_2$].

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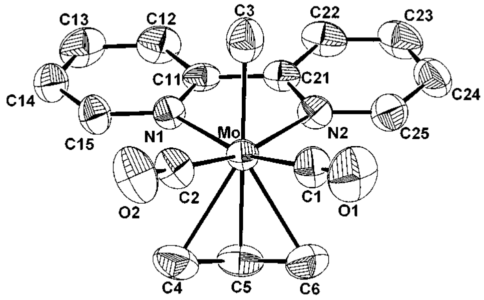

Figure 1. Molecular structure of **2a** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.[15]

of the new complexes indicate a composition of [Mo(R)(η^3-allyl)(CO)$_2$(N−N)], and a structure like that of **2a**. These compounds are the first [Mo(R)(η^3-allyl)(CO)$_2$L$_2$] derivatives and add to the very few examples of alkyl carbonyl molybdenum compounds without cyclopentadienyl ligands.[10]

Attempts to grow crystals from several non-chlorinated solvents led to microcrystalline materials unsuitable for single-crystal X-ray analyses. Single crystals grown by slow hexane diffusion into dichloromethane solutions of **2a** and **3a** at 250 K were found to consist of mixtures of the alkyl and the corresponding chloro-complex.[11] The {Mo(η^3-allyl)(CO)$_2$(N−N)} fragments of the Mo−CH$_3$ and Mo−Cl compounds of each pair were found to be, within the precision level of the results, identical. The disorder due to the partial occupancy of one site by the CH$_3$ and Cl ligands could be modeled to a reasonable degree, and the results[6] (Figure 1) were found to confirm the structure proposed on the basis of spectroscopic analysis.

All six new alkyl complexes are stable in non-chlorinated solvents (the ^{1}H NMR of **3a** remains unchanged after 1 week at room temperature in a d_6-acetone solution), and are moderately sensitive toward air and moisture. Thermal activation (refluxing tetrahydrofuran, 6 h) did not cause elimination of alkyl−allyl coupling products. Probably, this reluctance to complete an allylic alkylation process reflects a high configurational stability that keeps the two hydrocarbyl ligands on distant sites of the molecule. The stability of ethyl complexes **2b** and **3b** toward β-elimination indicates lack of facile ligand-dissociation processes.[12] This would also account for the lack of reactivity toward an excess of trimethylphosphine.[13] Remarkably, PMe$_3$ (5 equiv, 70 h at room temperature) does not induce the migration of the alkyl group to the proximate CO ligands.

The new alkyl complexes do not react with weak acids such as methanol or phenylacetylene (5 equiv, 20 h in d_6-acetone solution at room temperature). With triflic acid or benzenethiol, selective protonation of the alkyl−molybdenum bond occurs, yielding [Mo(X)(η^3-allyl)(CO)$_2$(N−N)] (X = OTf, SPh) complexes and the alkane.[6]

This selectivity is remarkable, since the reaction of Mo(η^3-allyl) complexes with strong acids has been used to generate, through allyl protonation and loss of the resulting olefin ligand, a vacant coordination site.[14]

In summary, we have shown that the reaction of [MoCl(η^3-allyl)(CO)$_2$(N−N)] (N−N = bipy, phen) complexes with dialkylmagnesium reagents yields selectively the alkyl complexes [Mo(R)(η^3-allyl)(CO)$_2$(N−N)], which are rigid in solution, have a mutually trans disposition of the alkyl and allyl ligands, and do not undergo migration or elimination processes.

Work underway in this lab indicates that other carbon nucleophiles, such as acetylides, react with [MoCl(η^3-allyl)(CO)$_2$(L−L)] compounds to yield new Mo−C products. These results will be reported in a forthcoming publication.

Acknowledgment. Dedicated to Professor R. Usón on occasion of his 75th birthday. We thank Ministerio de Ciencia y Tecnología (Projects MCT-00-BQU-0220 and CICYT BQU2000-0219) for financial support, and for a predoctoral fellowship (to L.R.).

Supporting Information Available: Complete details for the synthesis of all compounds, spectroscopic data, and X-ray crystallographic data for [Mo(CH$_3$)(η^3-allyl)(CO)$_2$(bipy)] (**2a**) and [Mo(CH$_3$)(η^3-allyl)(CO)$_2$(phen)] (**3a**) (PDF); CIF data. This material is available free of charge via the Internet at http://pubs.acs.org..

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[15] X-ray data for **2a**, C$_{15}$H$_{13}$ClMoN$_2$O$_2$: crystal dimensions 0.23 × 0.13 × 0.07 mm^3, monoclinic, space group $P2_1/c$, a = 8.379 (4) Å, b = 13.572 (6) Å, c = 13.958 (5) Å, β = 102.78 (4)°, V= 1548 Å^3, Z = 4, T = 293(2) K; a total of 3030 unique reflections ($2\theta \leq 52°$) was measured. Full-matrix least-squares refinement on F^2 (225 variables) converged to R = 0.0616, $wR2$ = 0.1234.