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Molybdenum alkynyls as alkynyl transfer reagents†

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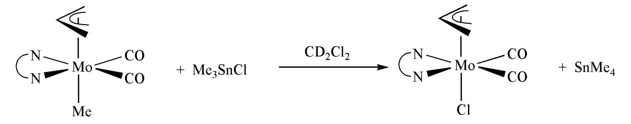
Molybdenum alkynyl complexes [Mo(C≡CR)(η^3-allyl)(CO)$_2$(phen)] feature long Mo–C$_{\text{alkynyl}}$ bond distances and propensity to undergo the cleavage of these bonds, a property that allowed their use as acetylide transfer reagents.

One of the more general methods for the creation of new transition metal–carbon bonds is the transmetallation reaction between a transition metal halide complex and an appropriate organometallic reagent.[1] To be of general usefulness, the latter should be sufficiently reactive and easily accessible. Organolithium and organomagnesium compounds are the reagents that best meet these criteria and therefore are widely employed in organometallic synthesis. However, since milder, more selective reagents are often required, organometallic compounds of tin, copper, mercury and other metals also find application.

Some examples of alkyl[2] and alkynyl[3] group transfer between transition-metal fragments are known; however, the main group derivatives are clearly more attractive synthetic reagents due to their easier preparation and lower cost. In addition, transmetallations using main group derivatives usually proceed to completion, a condition difficult to attain using transition metal compounds.

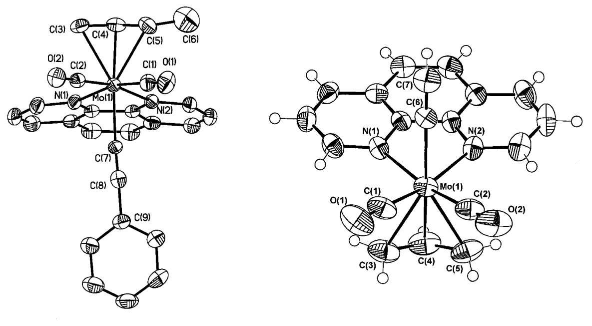
We have recently synthesized several alkyl and alkynyl complexes based on {Mo(η^3-allyl)(CO)$_2$(N–N)} fragments (N–N = 2,2′-bipyridine or 1,10-phenanthroline).[4] We have found that the reaction between equimolar amounts of [Mo(CH$_3$)(η^3-allyl)(CO)$_2$(phen)] and trimethyltin chloride in CD$_2$Cl$_2$ at room temperature yields a mixture of tetramethyltin and [MoCl(η^3-allyl)(CO)$_2$(phen)][5] (Scheme 1). Therefore, [Mo(CH$_3$)(η^3-allyl)(CO)$_2$(phen)] acts as a methylating agent stronger than tetramethyltin.[6]



Scheme 1

This prompted us to examine the capability of [Mo(C≡CPh)(η^3-allyl)(CO)$_2$(bipy)] (**1**)[4] to act as an alkynyl transfer reagent, and we found that trimethyltin chloride is cleanly converted to Me$_3$SnC≡CPh, establishing **1** as an alkynylation reagent superior to trimethyltin phenylacetylide.[7] It should be noted that **1** is a crystalline, non-hygroscopic solid that can be weighed in the air and can be prepared in a straightforward manner. In addition, it is synthesized from inexpensive starting materials and neither molybdenum nor the ancillary ligands have been attributed a high toxicity.

The structure of **1** has been previously determined by X-ray diffraction, but the low quality of the crystals severely limited the accuracy of the results.[4] We were interested in having more precise metrical data and, hence, high-quality single crystals of [Mo(C≡CPh)(η^3-crotyl)(CO)$_2$(phen)](**2**)[8] and [Mo(C≡CH)(η^3-allyl)(CO)$_2$(phen)] (**3**)[9] were subjected to X-ray diffraction analyses, giving the results shown in Figs. 1a and 1b respectively.



(a) **(b)**

Fig. 1 (a) Molecular structure and numbering scheme of **2** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–C(7) 2.188(4), C(7)–C(8) 1.140(6), C(8)–C(9) 1.479(7); C(8)–C(7)–Mo(1) 176.1(4), C(7)–C(8)–C(9) 179.0(5). (b) Molecular structure and numbering scheme of **3**. Selected bond lengths (Å) and angles (°): Mo(1)–C(6) 2.176(4), C(6)–C(7) 1.166(6); C(7)–C(6)–Mo(1) 177.9(4).

The structural features of greater interest to us here are the long Mo–C$_{\text{alkynyl}}$ and short C≡C distances,[10] which are consistent with negligible π-acceptor character of the acetylide moiety and lack of significant multiple character of the molybdenum–carbon bond in these complexes. This assimilates the [Mo(C≡CR)(η^3-allyl)(CO)$_2$(N–N)] compounds to the acetylides of the main group elements, which are incapable of back donation. This can be correlated with the ease with which these molybdenum reagents transfer the acetylide group. However, it would be unrealistic to forget that the outcome of the reaction must be the result of a balance where the relative solubilities of reagents and products may play a significant role.[11] In this regard, the very low solubility of the product [MoCl(η^3-allyl)(CO)$_2$(N–N)] in organic solvents of moderate polarity is likely to be part of the reaction driving force.

We have begun to explore the potential of these molybdenum compounds as practical alkynylation reagents in organometallic synthesis. Thus, **1** reacts with [Re(OTf)(CO)$_5$] to give [Re(C≡CPh)(CO)$_5$] (**4**), for which a good synthetic procedure was not available,[12] and [Mo(OTf)(η^3-allyl)(CO)$_2$(bipy)][4] (Scheme 2).

The products could be cleanly separated by repeated extractions of the alkynyl rhenium complex in a CH$_2$Cl$_2$–hexane mixture, in which the molybdenum triflato complex is insoluble.[13]

The relatively labile triflate group was needed for the reaction to proceed, since no reaction was observed using [ReCl(CO)$_5$]. This should not be taken as meaning that **1** is too weak an

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† Electronic supplementary information (ESI) available: Experimental section and crystal data for **2** and **3**. See http://www.rsc.org/suppdata/cc/b1/b110864f/

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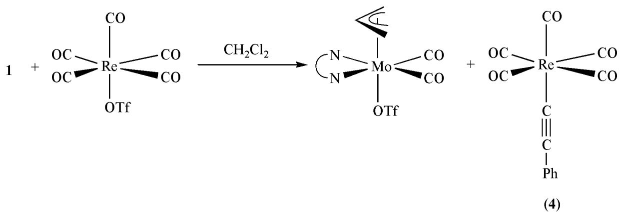
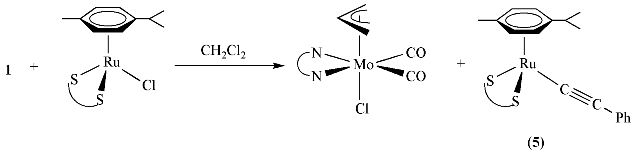


Scheme 2

alkynyl transfer reagent, since (a) the reaction of $[ReCl(CO)_5]$ with the strong alkylation reagent methyllithium affords the acetyl complex $[ReCl\{C(O)CH_3\}(CO)_4]^-$ rather than the CH_3/Cl exchange product,[14] and (b) the substitution of the triflate ligand in $[Re(OTf)(CO)_5]$ does not take place as easily as in typical triflato complexes.[15]

Areneruthenium alkynyls are attractive synthetic targets.[16] Complex **1** reacts with [RuCl(S–S)(η^6-*p*-cymene)](S–S=$S_2P(OEt)_2$)[17] to afford the new alkynyl complex [Ru(C≡CPh)(S–S)(η^6-*p*-cymene)] (**5**) (Scheme 3), characterized spectroscopically, and that could be isolated by silica gel chromatography.[18]



Scheme 3

The application of [Mo(C≡CR)(η^3-allyl)$(CO)_2$(N–N)] complexes to new organometallic syntheses is being studied in this laboratory.

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5 Details are given in the ESI†.

6 For examples of $SnMe_4$ as alkylating reagents , see: R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769.

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8 Crystal data for **2**: $C_{26}H_{20}MoN_2O_2$, M = 488.38, deep red prism (0.21 × 0.18 × 0.11 mm), triclinic, $P\bar{1}$, a = 10.720(1) Å, b = 10.985(1) Å, c = 11.313(1) Å, α = 62.64(1)°, β = 73.91(1)°, γ = 67.952(2)°, V = 1087.8(1) Å^3, Z = 2, D_{calc} = 1.491 g cm^{-3}, μ(Mo-Kα) = 0.628 mm^{-1}, Bruker AXS SMART 1000 CCD diffractometer, Mo-Kα radiation (λ = 0.71073 Å). 3099 independent reflections, 2804 observed ($I > 2\sigma(I)$). R_1 = 0.0371; wR_2 = 0.1096 for all reflections. CCDC 174912. See http://www.rsc.org/suppdata/cc/b1/b110864f/ for crystallographic files in .cif or other electronic format.

9 Crystal data for **3**: $C_{19}H_{14}MoN_2O_2$, M = 398.26, red prism (0.33 × 0.10 × 0.10 mm), monoclinic, $P2_1/c$, a = 7.276(5) Å, b = 13.562(6) Å, c = 16.759(7) Å, β = 90.74(11)°, V = 1653.6(14) Å^3, Z = 4, D_{calc} = 600 g cm^{-3}, μ(Mo-Kα) = 0.806 mm^{-1}, Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.71073 Å). 3231 independent reflections, R_1 = 0.0332; wR_2 = 0.0763 for 2119 observed ($I > 2\sigma(I)$). CCDC 174913.

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13 To a solution of **1** (0.090 g, 0.20 mmol) in CH_2Cl_2 (20 mL) was transferred a solution of $[Re(OTf)(CO)_5]$ (0.095 g, 0.20 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 12 h at rt. The solvent was evaporated to dryness and the residue was extracted with CH_2Cl_2–hexane (1:3 ratio; 3 × 10 mL). A light yellow solution of $[Re(C{\equiv}CPh)(CO)_5]$ (**4**) and a red residue of [Mo(OTf)(η^3-C_3H_5)$(CO)_2$(bipy)] were obtained. The solution of **4** was evaporated under vacuum, the residue was washed with cold hexane (at 0 °C, 3 × 5 mL) and **4** was obtained as a light yellow solid. The residue of [Mo(OTf)(η^3-C_3H_5)$(CO)_2$(bipy)] was washed with hexane (3 × 10 mL) and dried under vacuum. Both compounds were characterized spectroscopically: $[Re(C{\equiv}CPh)(CO)_5]$ (**4**). Yield: 0.041 g, 48%. IR(CH_2Cl_2): 2118 ($\nu_{C\equiv C}$), 2149, 2036, 1994(ν_{CO}). ^{1}H NMR($CDCl_3$): 7.36 [m, 2H, Ph], 7.25 [m, 3H, Ph]. $^{13}C\{^1H\}$ NMR($CDCl_3$): 180.01 [CO], 131.80, 128.89, 128.36 and 127.34 [Ph], 112.70 [C_α], 80.63 [C_β]. [Mo(OTf)(η^3-C_3H_5)(CO-)$_2$(bipy)]. IR(CH_2Cl_2): 1951, 1865 (ν_{CO}). ^{1}H NMR(CD_2Cl_2): 9.18, 8.19, 8.11 and 7.69 [m, 2H each, bipy], 4.04 [m, 1H, H_c], 3.76 [d (6.6 Hz), 2H, H_{syn}], 1.59 [d (9.6 Hz), 2H, H_{anti}]. $^{19}F\{^1H\}$NMR (CD_2Cl_2): −79.27.

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18 To a solution of **1** (0.100 g, 0.22 mmol) in CH_2Cl_2 (15 mL) was added a solution of $[RuCl\{S_2P(OEt)_2\}$(η^6-*p*-cymene)] (0.063 g, 0.14 mmol) in CH_2Cl_2 (15 mL). The resulting slurry was stirred for 12 h. The solvent was evaporated *in vacuo*, the residue was extracted with a CH_2Cl_2–hexane mixture (1:2 ratio; 3 × 10 mL) and the resulting orange solution was filtered through silica gel. The volatiles were removed under *vacuo* and compound **5** was obtained as a dark orange solid. [Ru(C≡CPh)-$\{S_2P(OEt)_2\}$(η^6-*p*-cymene)](**5**). Yield: 0.072 g, 63%. IR(CH_2Cl_2): 2096 ($\nu_{C\equiv C}$). ^{1}H NMR($CDCl_3$): 7.19 [m, 5H, C_6H_5], 5.47, 5.44, 5.24 and 5.21 [qAB, 4H, C_6H_4], 4.17 [m, 4H, OCH_2CH_3], 2.91 [m, 1H, $CH(^iPr)$], 2.22 [s, 3H, CH_3-C_6H_4], 1.37 [t (7.1 Hz), 3H, OCH_2CH_3], 1.31 [d (6.9 Hz), 6H, $CH_3(^iPr)$], 1.20 [t (7.1 Hz), 3H, OCH_2CH_3]. $^{31}P\{^1H\}$ NMR($CDCl_3$): 107.64. $^{13}C\{^1H\}$ NMR(CD_2Cl_2): 131.33, 129.35, 128.23 and 124.74 [C_6H_5], 114.02 [C_α], 106.90 [C_m], 105.75 [C_β], 103.14 [C_i], 85.78 [C_A], 85.48 [C_B], 64.41 [OCH_2CH_3], 63.22 [OCH_2CH_3], 31.75 [$CH(^iPr)$], 22.88 [$CH_3(^iPr)$], 19.28 [CH_3-C_6H_4], 16.30 [OCH_2CH_3]. The residue insoluble in the CH_2Cl_2 mixture was washed with hexane (3 × 5 mL), dried *in vacuo* and identified (IR and ^{1}H NMR) as [MoCl(η^3-C_3H_5)$(CO)_2$(bipy)].