Notes

Tricarbonyltris(pyridine)molybdenum: A Convenient Reagent for the Preparation of (π-Allyl)molybdenum Complexes

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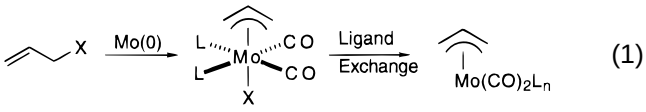
Summary: The reaction of tricarbonyltris(pyridine)molybdenum(0) with various allylic substrates provides easy access to the corresponding (π-allyl)molybdenum(II) complexes in high yields under variable conditions.

The use of transition metals in the synthesis of complex organic molecules is a growing field of interest. The activating, stabilizing, and directing effects of various metals constitute powerful tools for functional-group manipulation and have been applied to organic synthesis.[1]

A lot of effort has been directed toward the preparation and application of (π-allyl)molybdenum complexes, which can be obtained by reacting allylic halides,[2] acetates,[3] or phosphinates[4] with a corresponding molybdenum(0) source (eq 1); compounds **1** and **2** are commonly used.



(1)

X = Cl, Br, I, OAc, $OP(O)R_2$; L = CH_3CN, DMF, py; L_n = Cp, Tp;[8]
Mo(0): $Mo(CO)_3(CH_3CN)_3$ (**1**);[5] $Mo(CO)_3(DMF)_3$ (**2**);[6] $Mo(CO)_3(py)_3$ (**3**).[7]

In need of a reliable protocol for the preparation of various π-allyl complexes, we have found that tricarbonyltris(pyridine)molybdenum (**3**) is a convenient reagent for such purposes. In 1935, Hieber and Mühlbauer prepared complex **3** for the first time and isolated it as an air-stable, yellow, crystalline solid.[7] Since then, compound **3** has been mainly used for the synthesis of η^6-arene complexes in the presence of a Lewis acid, not, however, for the corresponding η^3-complexes. Hayter, who established an early route to π-allyl intermediates by using the tris(acetonitrile) complex **1**, stated that "an analogous series of complexes may also be obtained by treating $Mo(CO)_3(py)_3$ with allylic halides, but this synthesis is less satisfactory".[2] In contrast to these findings, we have successfully employed complex **3** as a convenient Mo(0) source for the synthesis of various known and new π-allyl compounds. It is easily prepared in high yield (92%),[7] has a good shelf-life and stability in solution, and thus, is more practical to use than the corresponding acetonitrile or DMF complex. Although tricarbonyltris(acetonitrile)molybdenum (**1**) can be conveniently prepared *in situ*,[5] it is very air-sensitive and unstable in solvents other than acetonitrile. Employing the DMF complex (**2**),[6] we experienced difficulties in preparing and handling the reagent which easily deteriorated under Schlenk line conditions.

The results for the practical application of tris(pyridine)molybdenum in comparison with tris(acetonitrile)molybdenum are summarized in Table 1, indicating competitive yields for the new route (62−99%). A variety of allylic substrates (**4**−**11**, *i.e.*, chloride, bromide, acetate; Chart 1) were reacted with complexes **1** and **3** to give rise to the corresponding molybdenum complexes **12**−**19** (Chart 2) as mostly air-stable, yellow, orange, red, or brown solids. During the oxidative-addition reaction of complex **3**, the conditions can be varied according to substrate reactivity by changing the solvent as well as the reaction time and temperature. Complex **3** is more soluble in benzene and dichloromethane than in ether, which was used for fast reacting substrates at reflux. It was also effective at room temperature when reacted in benzene (entry 9) or dichloromethane (entry 10). In addition, the use of complex **3** tolerated functionalized substrates, *e.g.*, ester and acetonide groups (entries 8, 9, 11−13) and even provided conversion of allylic acetates (entries 2, 7, 11), which are usually less reactive. Reactions of complex **1**, although reasonably successful when allylic chlorides and bromides were used, gave poor results with the corresponding acetates (entries 2, 7, 11). Conversion of substrates **11b**−**d** (entries 11−13), which contain a stereogenic center, gave rise to isomeric mixtures of complex **19** (1:1 to 3:1 by ^{1}H NMR). Surprisingly, one of the isomers is unstable and selectively decomposes upon storage, providing the stable diastereomer in high purity (95% by ^{1}H NMR).

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(1) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.
(2) Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, P1−P3.
(3) (a) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132−4256. (b) Villanueva, L. A.; Ward, Y. D.; Lachiotte, R.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4190−4200.
(4) McCallum, J. S.; Sterbenz, J. T.; Liebeskind, L. S. *Organometallics* **1993**, *12*, 927−932.
(5) (a) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433−434. (b) King, R. B. *J. Organomet. Chem.* **1967**, *8*, 139−148.
(6) Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Gazz. Chim. Ital.* **1992**, *122*, 275−277.
(7) Hieber, W.; Mühlbauer, F. *Z. Anorg. Allg. Chem.* **1935**, *221*, 337−348.
(8) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497. (c) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17. (d) Trofimenko, S. *J. Am Chem. Soc.* **1069**, *91*, 588.
(9) Ipaktschi, J.; Hartmann, A.; Boese, R. *J. Organomet. Chem.* **1992**, *434*, 303−320.

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Table 1. Preparation of (π-Allyl)molybdenum Complexes[a]

entry	substrate	product	$Mo(CO)_3(py)_3$(**3**)[b]	$Mo(CO)_3(MeCN)_3$(**1**)[c]	other Mo(0)
1	**4a**	**12**	85[d,e]	76[d]	68[f]
2	**4b**	**12**	73[d]	9[d]	77[g]
3	**5**	**13**	79[d]	89[h]	92[g]
4	**6a**	**14**	72[i,j]	65[i]	
5	**6b**	**14**			57[g,k]
6	**7**	**15**	70[e]	64	
7	**8**	**16**	99[h,l]	23[h,m]	91[g]
8	**9a**	**17a**	76[e,j]		61[g]
9	**9b**	**17b**	82[e],74[n]	93	
10	**10**	**18**	85[d,o],62[d,p]	89[d]	45[g],69[f]
11	**11b**	**19**	82[l]	11[m,q]	
12	**11c**	**19**	97[r]	66	
13	**11d**	**19**	88[e]	91	

[a] Substrates and products are depicted in Charts 1 and 2, respectively. [b] Method 1, 1.0 equiv of substrate, yields reported for two steps. [c] Method 2, 1.0 equiv of substrate, $Mo(CO)_3(MeCN)_3$ was prepared *in situ*, yields reported for three steps. [d] All spectroscopic data were in agreement with the reported literature values, see ref 9. [e] Step 1: Et_2O, reflux, 1 h. [f] Substrate (3 equiv) was reacted with $Mo(CO)_3(CH_3CONMe_2)_3$, see ref 9. [g] $Mo(CO)_3(DMF)_3$, see ref 3. [h] All spectroscopic data were in agreement with the reported literature values, see ref 3. [i] Predominantly *syn*-product, *syn*/*anti* >9:1; all spectroscopic data were in agreement with the reported literature values, see ref 3. [j] Step 1: Et_2O/CH_2Cl_2 (1:1), reflux, 1 h. [k] (*E*)- and (*Z*)-Crotyl bromide and 3-bromo-1-butene (1.5 equiv). [l] Step 1: PhH, reflux, 5 h. [m] Step 2: MeCN, reflux, 24 h. [n] Step 1: PhH, room temperature, 3 h. [o] Step 1: CH_2Cl_2, reflux, 2 h. [p] Step 1: CH_2Cl_2, room temperature, 18 h. [q] 72% starting material recovered. [r] Step 1: Et_2O, reflux, 4 h.

Chart 1

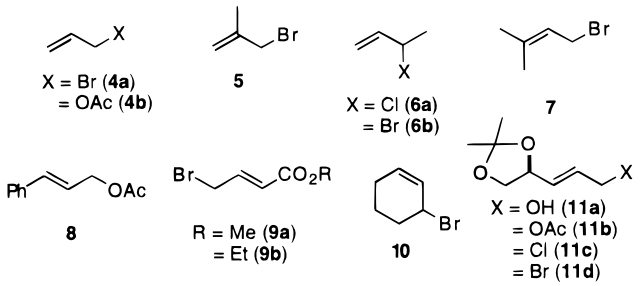
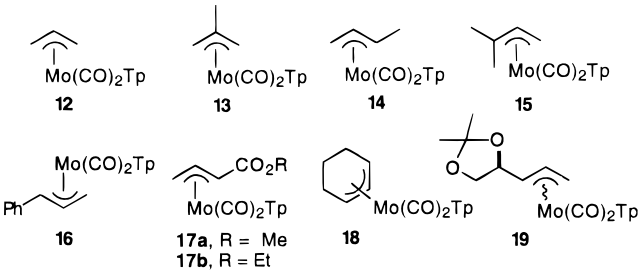


Chart 2



Tp = hydrotris(1-pyrazolyl)borate[8]

In conclusion, we have found that the use of tricarbonyltris(pyridine)molybdenum (**3**) provides easy access to the corresponding (π-allyl)molybdenum(II) complexes. The stability of complex **3** represents a considerable advantage over alternative Mo(0) sources and allows for easy handling under different reaction conditions. Despite its stability, tricarbonyltris(pyridine)molybdenum is sufficiently reactive to provide conversion of various allylic substrates in very good yields.

Experimental Section

All solvents used were freshly distilled under a nitrogen atmosphere as follows: Tetrahydrofuran, diethyl ether, and benzene from sodium/benzophenone; dichloromethane, pentane, and acetonitrile from calcium hydride. Triethylamine was distilled from calcium hydride and stored over molecular sieves, 4 Å. Hexacarbonylmolybdenum, allyl acetate and bromide, 3-bromo-2-methyl-propene, 3-chloro-1-butene, 4-bromo-2-methyl-2-butene, cinnamyl alcohol, methyl and ethyl 4-bromocrotonates, 3-bromocyclohexene, and sodium tris(1-pyrazolyl)-borohydride were purchased from Aldrich Chemical Co. Complexation reactions were carried out under a positive pressure of argon in oven-dried glassware. However, reactions described under Method 1 proceeded successfully without an inert atmosphere. All NMR spectral data were recorded on a Varian Gemini 300 spectrometer. Melting points were recorded on a Unimelt Thomas Hoover capillary melting-point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet Impact 400 spectrometer. Analytical thin-layer chromatography was performed on glass plates precoated with F_{254} silica gel 60 (Merck). Column or flash chromatographies were carried out using silica gel 60 (Baker, 200−400 mesh), alumina (Fisher Scientific, Neutral Brockman Activity I, 60−325 mesh), or Florisil (Acros, 100−200 mesh). All chromatograms were analyzed by ultraviolet illumination or visualization by one or more of the following: (1) phosphomolybdic acid, (2) potassium permanganate, (3) vanillin, or (4) iodine chamber.

Tricarbonyltris(pyridine)molybdenum (3). In a modified literature procedure,[7] hexacarbonylmolybdenum (4.00 g, 15.15 mmol) was reacted with freshly distilled pyridine (10 mL) by heating at 80 °C for 1 h and at 130 °C for an additional 2 h. The reaction mixture became dark red and was allowed to cool without stirring. Crystals formed, and precipitation was completed by adding pentane and cooling with an ice bath. The mixture was filtered, and the product was washed with pyridine and pentane to afford a yellow, crystalline solid (5.79 g, 92%).

(4*S*)-(*E*)-4,5-(Isopropylidenedioxy)-2-pentenyl Acetate (11b). A solution of allylic alcohol **11a** (50 mg, 0.316 mmol),[10] acetic anhydride (66 μL, 0.700 mmol), and pyridine (127 μL) in methylene chloride (2 mL) was stirred at room temperature for 24 h. Upon completion, the reaction mixture was quenched with NH_4Cl and diluted with diethyl ether. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated. Column chromatography (3:1, hexanes/ethyl acetate) provided the allylic acetate (50 mg, 79%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 3 H), 1.42 (s, 3 H), 2.06 (s, 3 H), 3.59 (dd, J = 7.7, 7.7 Hz, 1 H), 4.09 (dd, J = 6.2, 8.1 Hz, 1 H), 4.51 (ddd, J = 6.7, 7.3, 7.3 Hz, 1 H), 4.56 (bd, J = 5.5 Hz, 2 H), 5.74 (bddd, J = 1.3, 6.8, 15.5 Hz, 1 H), 5.88 (dt, J = 15.7, 5.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 20.8, 25.8, 26.6, 63.8, 69.2, 76.1, 109.4, 127.8, 131.5, 170.6. IR (neat): 2997, 2937, 2884, 1752, 1461, 1375, 1243, 1163, 1064, 1038, 978, 872 cm^{-1}.

General Halogenation Procedure. To a solution of alcohol **11a** (2.6 mmol, 1 equiv)[10] and NXS (X = Cl, Br, 3.4 mmol, 1.3 equiv) in THF was added Ph_3P (3.13 mmol, 1.2 equiv) at 0 °C. The cooling bath was removed, and the reaction continued for 4−7 h (monitored by TLC). Upon completion, the reaction mixture was quenched with water and diluted with hexanes/ethyl acetate (1:1, 150 mL). The organic layer was washed with brine, dried, filtered, and concentrated. Silica gel or Florisil chromatography (gradient 6:1 to 3:1, hexanes/ethyl acetate) provided the purified halides.

(4*S*)-(*E*)-4,5-(Isopropylidenedioxy)-2-penten-1-yl Chloride (11c). The allylic chloride was isolated as a colorless liquid (88%). ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 3 H), 1.42 (s, 3 H),

(10) Marshall, J. A.; Trometer, J. D.; Cleary, D. G. *Tetrahedron* **1989**, *45*, 391−402.

3.61 (dd, J = 7.7, 7.7 Hz, 1 H), 4.05 (d, J = 6.5 Hz, 2 H), 4.11 (dd, J = 6.1, 8.2 Hz, 1 H), 4.53 (ddd, J = 6.7, 6.9, 6.9 Hz, 1 H), 5.77 (dABq, J = 6.9, 15.4 Hz, 1 H), 5.94 (ddABq, J = 6.5, 6.5, 15.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 25.7, 26.6, 43.8, 69.2, 75.8, 109.5, 129.3, 132.0. IR (neat): 2990, 2942, 2879, 1379, 1247, 1226, 1163, 1066, 975, 863, 703 cm^{-1}.

(4*S*)-(*E*)-4,5-(Isopropylidenedioxy)-2-penten-1-yl Bromide (11d). The allylic bromide was isolated as a colorless liquid (75%). ^{1}H NMR ($CDCl_3$): δ 1.39 (s, 3 H), 1.43 (s, 3 H), 3.61 (dd, J = 7.8, 7.8 Hz, 1 H), 3.95 (d, J = 7.4 Hz, 2 H), 4.12 (dd, J = 6.2, 8.2 Hz, 1 H), 4.53 (ddd, J = 6.9, 7.0, 7.0 Hz, 1 H), 5.78 (dABq, J = 7.0, 15.0 Hz, 1 H), 6.01 (ddABq, J = 7.1, 7.1, 15.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 25.8, 26.6, 31.3, 69.2, 75.8, 109.6, 129.7, 132.5. IR (neat): 2992, 2944, 2889, 1443, 1374, 1223, 1162, 1073, 970, 860 cm^{-1}.

Complexation Method 1. Complex **3** was reacted with the corresponding allylic substrate (0.1−0.3 mmol, 1.0 equiv) in Et_2O, CH_2Cl_2, or PhH (2−5 mL) at various temperatures (20−100 °C, see Table 1). The progress of the reaction was monitored by TLC (1−6 h). Upon completion, the solvent was removed *in vacuo* and the residue dissolved in THF (2−5 mL). To the reaction mixture was added sodium hydrotris(1-pyrazolyl)borate (NaTp, 1.0 equiv) at room temperature, and the ensuing ligand exchange (3−24 h) provided the corresponding π-allyl complex. The crude product was purified by filtration through a plug of alumina (CH_2Cl_2), followed by crystallization or column chromatography.

Complexation Method 2. In a typical procedure, complex **1** was prepared *in situ* by refluxing hexacarbonylmolybdenum (0.2−0.7 mmol, 1 equiv) in acetonitrile (2−6 mL) for 1−3 h under an inert atmosphere.[5] A solution of the allylic substrate (1.0 equiv) was added at elevated temperatures (50−80 °C) and reacted for 0.5−24 h. Upon completion, the reaction mixture was allowed to cool and concentrated *in vacuo*. The residue was dissolved in THF and stirred with sodium hydrotris(1-pyrazolyl)borate (NaTp, 1.0 equiv) at room temperature (3−24 h) to afford the corresponding complex; purification was carried out as in Method 1.

Dicarbonyl[tris(1-pyrazolyl)borato](η^3-3-methyl-2-buten-1-yl)molybdenum (15). The complex was isolated as a yellow solid, mp 184 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 3 H), 1.87 (dd, J = 3.8, 9.9 Hz, 1 H), 1.91 (s, 3H), 3.52 (dd, J = 3.8, 7.11 Hz, 1 H), 3.92 (dd, J = 7.1, 9.8 Hz, 1 H), 6.20 (bs, 3 H), 7.80 (br, 3 H). ^{13}C NMR ($CDCl_3$): δ 23.2, 28.6, 47.4, 82.0, 99.9, 105.3, 135.6, 145.4, 230.7, 233.5. IR (CH_2Cl_2): 2491, 1928, 1830, 1414, 1316, 1227, 1137, 1055, 770, 729 cm^{-1}. HREIMS: m/e calcd for $C_{16}H_{19}BMoN_6O_2$ (M^+), 436.07176; found, 436.07166.

Dicarbonyl[tris(1-pyrazolyl)borato][η^3-1-(carboxyethyl)-2-propen-1-yl]molybdenum (17b). Isolated as a yellow solid; mp 140 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.06 (t, J = 7.1 Hz, 3 H), 1.45 (dd, J = 2.6, 9.8 Hz, 1 H), 2.54 (d, J = 9.6 Hz, 1 H), 3.67 (dd, J = 2.6, 7.1 Hz, 1 H), 3.86−4.08 (m, 2 H), 4.86 (ddd, J = 7.1, 9.7, 9.7 Hz, 1 H), 6.19 (t, J = 2.1 Hz, 3 H), 7.54 (d, J = 2.2 Hz, 3 H), 7.94 (br, 2 H), 8.40 (br, 1 H). ^{13}C NMR ($CDCl_3$): δ 13.8, 47.9, 60.2, 67.2, 86.5, 105.5, 135.5, 143.7, 171.7, 225.2, 235.2. IR (CH_2Cl_2): 3141, 2990, 2937, 2498, 1969, 1870, 1719, 1515, 1417, 1311, 1053, 774, 728 cm^{-1}. HREIMS: m/e calcd for $C_{17}H_{19}BMoN_6O_4$ (M^+), 480.06159; found, 480.06149.

Dicarbonyl[tris(1-pyrazolyl)borato][η^3-(4*S*)-4,5-(isopropylidenedioxy)-2-penten-1-yl]molybdenum (19). The stable isomer was isolated as a yellow solid; mp 140 °C. ^{1}H NMR ($CDCl_3$): δ 1.06 (dd, J = 3.2, 8.8 Hz, 1 H), 1.44 (s, 3 H), 1.54 (s, 3 H), 2.19 (dd, J = 9.4, 9.4 Hz, 1 H), 3.42 (dd, J = 3.1, 6.5 Hz, 1 H), 3.72 (ddd, J = 6.5, 8.9, 8.9 Hz, 1 H), 3.88 (dd, J = 7.8, 7.8 Hz, 1 H), 4.20 (dd, J = 6.0, 7.7 Hz, 1 H), 4.33 (ddd, J = 5.9, 8.3, 8.3 Hz, 1 H), 6.2 (bs, 3 H), 7.56 (bs, 3 H), 8.40 (br, 3 H). ^{13}C NMR ($CDCl_3$): δ 25.6, 26.7, 47.5, 71.9, 74.0, 76.3, 82.4, 105.4, 109.6, 135.5, 144.5, 225.3, 232.8. IR (CH_2Cl_2): 2993, 2492, 1943, 1854, 1512, 1423, 1224, 1135, 1059, 771, 730 cm^{-1}. HREIMS: m/e calcd for $C_{19}H_{23}BMoN_6O_4$ (M^+), 508.09289; found, 508.09277. The isomeric mixture was obtained as a yellow to brown oil. Data for the less stable isomer was obtained from the mixture. ^{1}H NMR ($CDCl_3$): δ 1.39 (s, 3 H), 1.52 (s, 3 H), 1.71 (bd, J = 9.3 Hz, 1 H), 1.93 (dd, J = 6.7, 9.8 Hz, 1 H), 3.56 (dd, J = 1.7, 6.8 Hz, 1 H), 4.06 (dd, J = 6.3, 8.1 Hz, 1 H), 4.38−4.44 (m, 2 H), 4.82 (ddd, J = 6.2, 6.3, 6.3 Hz, 1 H), 6.22 (bs, 3 H), 8.06 (bs, 3 H), 8.63 (br, 3 H). ^{13}C NMR ($CDCl_3$): δ 25.4, 27.0, 55.6, 70.5, 76.1, 76.4, 80.2, 105.5, 109.3, 144.5, 146.0 229.6, 231.4.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **15**, **17b**, and **19** (6 pages). Ordering information is given on any current masthead page.

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