# Synthesis and Structure of New Molybdenum π-Allyl Complexes: Unexpected Hydrolysis of Tris(3,5-dimethyl-1-pyrazolyl)phosphine Oxide†

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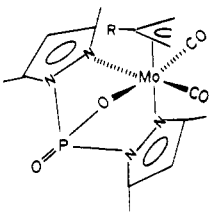
The reaction of tris(3,5-dimethyl-1-pyrazolyl)phosphine oxide (1) with $(CH_3CN)_2(CO)_2MoX(\eta^3\text{-}CH_2CHRCH_2)$ (**3a–d**; R = H, $CH_3$, Ph; X = Cl, Br) gave products **4a–c** (R = H, $CH_3$, Ph) in which the ligand 1 was partially hydrolyzed. The proton NMR spectra of complexes **4a–c** were dynamic due to



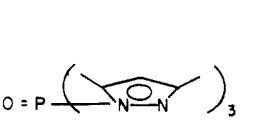
**4a–c**

nonrigidity of these molecules. The structure of the complex **4c** (R = Ph) was established by X-ray diffraction. The compound $C_{21}H_{23}MoPO_4N_4$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a$ = 10.013 (1) Å, $b$ = 14.154 (2) Å, $c$ = 15.951 (2) Å, $V$ = 2260.7 (5) Å$^3$, $Z$ = 4, and $\rho$(calcd) = 1.77 g cm$^{-3}$. With use of Cu K$\alpha$ radiation, for 1842 observed reflections ($\omega$–$2\theta$ mode, maximum $\theta$ = 60°), the structure was refined to $R$ = 0.0817; the largest shift/esd was 0.08. The crystal structure showed that one pyrazole group was replaced by oxygen; the oxygen was placed cis to the allyl group. EHMO calculations indicated that such a conformation was more stable than the one where oxygen was trans to the allyl group.

## Introduction

There has been longstanding interest in the structure and reactivity of molybdenum π-allyl compounds.[1] The regiochemistry of nucleophilic attack on a metal-bound allyl group has been extensively studied.[2] Molybdenum-catalyzed allylation reactions are currently being pursued,[3] and a large number of stereochemically nonrigid allyl complexes have been studied with use of dynamic NMR spectroscopy.[4] On the other hand, there has been an ever-increasing interest in the polypyrazolylborate ligands and their analogues[5] during the last two decades, since Trofimenko introduced them in the 1960s. These ligands provide air- and moisture-stable substances of a wide structural variety and often permit isolation and characterization of stable odd-electron complexes.[6]

In pursuance of our interest in ligand-modified reactivity of organometallics with particular interest in polypyrazolyl chelates, we wish to report the preparation, structure, and stereochemical nonrigidity of a new class of molybdenum π-allyl compounds.[7] Tris(3,5-dimethyl-1-pyrazolyl)-phosphine oxide (1) was chosen as a tridentate chelating ligand; its synthesis was reported,[8] but its use in organometallic or coordination chemistry remained unexplored. A tripodal structure with three N-donors and a competing



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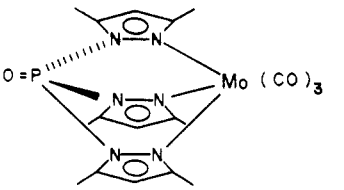

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binding site at oxygen were thought to have interesting structural implications in the metal complexes.

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† NCL Communication No. 4998.

‡ To whom enquiries regarding the X-ray structure should be addressed.

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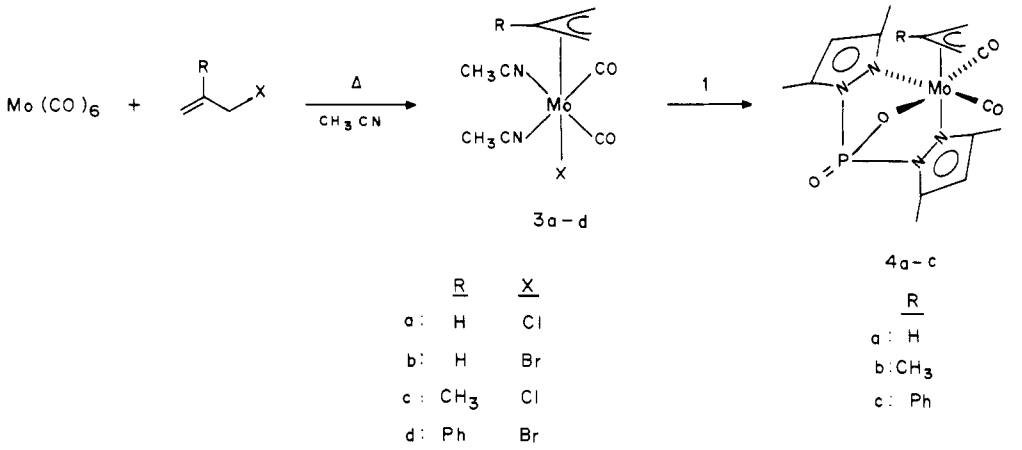
**Scheme I**




| | R | X |
|---|---|---|
| a: | H | Cl |
| b: | H | Br |
| c: | $CH_3$ | Cl |
| d: | Ph | Br |

| | R |
|---|---|
| a: | H |
| b: | $CH_3$ |
| c: | Ph |

**Table I. Infrared and Microanalytical Data[a]**

| compd | color | yield, % | IR, $cm^{-1}$ [b] | | | anal. found[c] (calcd) | | |
|---|---|---|---|---|---|---|---|---|
| | | | CO | CN | PO | C | H | N |
| **2** | yellow | 58 | 1950<br>1850 | 1560 | 1180 | 42.15<br>(42.18) | 4.05<br>(4.10) | 16.27<br>(16.40) |
| **4a** | orange | 52 | 1940<br>1840 | 1560 | 1180 | 40.06<br>(40.35) | 4.17<br>(4.25) | 12.04<br>(12.55) |
| **4b** | yellow | 44 | 1925<br>1830 | 1560 | 1180 | 41.74<br>(41.75) | 4.58<br>(4.56) | 12.10<br>(12.17) |
| **4c** | orange | 23 | 1940<br>1850 | 1560 | 1180 | 48.27<br>(48.27) | 4.38<br>(4.40) | 10.76<br>(10.72) |

[a] All of the compounds in the table have melting points >250 °C (with decomposition). [b] Nujol mull. [c] We wish to thank Perkin-Elmer, Bio-nics, and Leco Corp. (USA) and CSMCRI (India) for the analytical results.

**Table II. $^1H$ NMR Data for Compounds 4a–c in $CDCl_3$[a]**

| complex | conditions | allyl protons | | | substitution | | pyrazole | |
|---|---|---|---|---|---|---|---|---|
| | | syn, 2 H | central, 1 H | anti, 2 H | $CH_3$ | $C_6H_5$ | 4-H, 2 H | 3(5)-$CH_3$, 12 H |
| **4a** | 90 MHz, 223 K | 3.3–3.9 m[b] | | 1.4 d<br>1.7 d | | | 5.9 dd | 2.9 s<br>2.45 s<br>2.4 bs |
| **4b** | 300 MHz, 260 K | 3.5 bs<br>3.2 bs | | 1.46 bs<br>1.35 bs | 2.83 | | 6.0 bs<br>5.9 bs | 2.45 s<br>2.4 s |
| **4c** | 300 MHz, 255 K | 4.2 bs<br>3.9 bs | | 1.45 bs | | 7.25 m<br>7.05 m | 5.9 d<br>5.75 d | 2.8 s<br>2.5 s<br>2.25 s<br>2.1 s |

[a] Coalescence is observed for all signals except the allyl substituent. [b] Signal for syn and central protons of the allyl group.

## Results and Discussion

The ligand 1 was prepared by a modified procedure from $POCl_3$ and 3,5-dimethylpyrazole with triethylamine as a base in refluxing benzene and purified by crystallization from $CCl_4$–petroleum ether. The compound was hygroscopic and slowly decomposed on storage. It could be preserved, however, under petroleum ether without any change for several months. The crystals were collected by filtration and dried before use. Treatment of this compound with $Mo(CO)_6$ in boiling acetonitrile gave the complex **2**. This complex did not react with allyl halides readily. Therefore, the allyl compounds were sought to be prepared by ligand exchange with a preformed Mo–allyl complex.

The usual protocol[9] was followed for the preparation of the compound **3** with use of the appropriate allyl halide (Scheme I). The ligand 1 was added either to the refluxing acetonitrile solution of the parent complexes **3a–d** or to the same solution at room temperature under argon followed by heating under reflux for 10 min. Concentration

(4) (a) See reference 1a and refs 1–4 therein. (b) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 3183.
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**Table III. $^{13}C$, $^{31}P$,[a] and $^{95}Mo$[b] NMR Data**

| compd | CO | allyl terminal C | allyl central C | allyl $CH_3$ | allyl Ph | pyrazole C3 | pyrazole C4 | pyrazole C5 | pyrazole C4–R | $^{31}P$ | $^{95}Mo$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2** (solid) | 234.4<br>232.4<br>231.1<br>229.1<br>227.5 | | | | | 161.5 | 112.3<br>108.9 | 151.9<br>150.2 | | | |
| **4a** | 228.6<br>227.4 | 55.2<br>65.3 | 78.6 | | | 155.8<br>157.2 | 109.5 | 146.2<br>147.4 | 14.3<br>11.5 | -12.09 | -787.6 |
| **4b** | 226.9<br>228.2 | 59.4 (broad) | 88.4 | 19.6 | | 156.1 | 109.5 | 146.6 | 14.2<br>11.4 | -12.13 | -746.5 |
| **4c** | 227.4<br>225.1 | 55.1<br>57.4 | 85.3 | | 154.5<br>135.9<br>126.6<br>124.3 | 156.5 | 109.1 | 147.1 | 14.1<br>11.1 | -12.46 | -762.3 |

[a] Conditions: 121.6 MHz, $CDCl_3$, 85% $H_3PO_4$ as external standard. [b] Conditions: 19.554 MHz, $CDCl_3$, 2 M $Na_2MoO_4$ as external standard, line width 330–500 Hz.

of the solution in vacuo and addition of water precipitated a solid that could be recrystallized from aqueous acetonitrile as long orange-yellow needles. The characteristic IR bands for the CO, C=N, and P=O groups (Table I) appeared consistent with the expected product.

The proton NMR spectra of all the compounds (Table II) recorded at room temperature showed considerable line broadening. The spectra of the products derived from **3a** and **3b** were identical; the spectrum of the compound derived from **3c** showed relatively sharp features depicting rapid exchange of conformations. The averaged spectra obtained above room temperature featured singlets for the pyrazole (4-H and 3- and 5-$CH_3$) as well as singlets for the syn and anti protons of the 2-substituted allyl group (or doublets for the syn and anti protons and a multiplet for the central proton of an unsubstituted allyl group). When the compounds are cooled, all these signals broaden and finally split into two sets each. However, for a tridentate ligand, the ratio of the nonequivalent pyrazole signals should have been 2:1. But in all the cases, the observed ratio was 1:1. Further, due to the symmetry of the tridentate ligand, the allyl signals were expected to remain unchanged despite the temperature variation; even these were split into two sets of equal intensity, indicating a loss of symmetry in the molecule.

The X-ray crystal structure[10] of the 2-phenylallyl derivative revealed that one of the pyrazoles had been hydrolyzed from the tridentate ligand and the actual structure was as shown in Figure 1. In light of this, the structures of the new compounds were formulated as **4a–c**.

Certain deformities in the structure are noteworthy. The central carbon of the allyl group is slightly tilted toward the metal, and the aromatic ring is further bent toward the metal by about 10° (a tilt away from the metal is said to be more common[11]). The aromatic ring is also twisted off the allyl plane, as seen from the dihedral angles. Both the P–O bonds are of equal length, with the O–P–O angle at 126°.

The crystal structure provided what we may presume to be the preferred conformation of these complexes. The allyl group, as seen from Figure 1, is trans to one of the

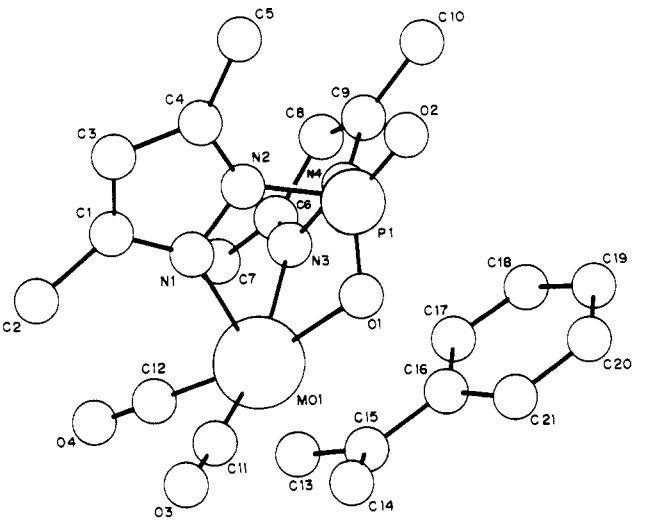
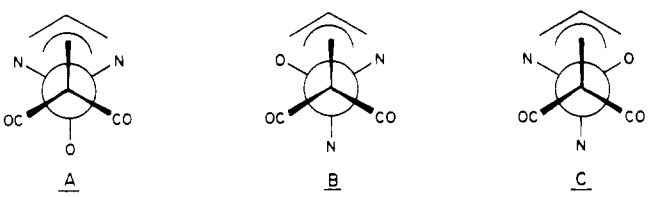



**Figure 1.** PLUTO diagram for the molecule **4c**.

**Chart I**




pyrazolyl groups and cis to the oxygen donor, which is to be expected since the strong $\pi$-acid CO would prefer the stronger donor O=P—$O^-$ in the trans position.[7] The orientation of the allyl group with respect to the two carbon monoxide ligands in **4c** conforms to related structures and is also in agreement with the predicted stable conformation based on EHMO calculations.[12] As postulated by Shiu,[7] the three possible conformers A–C (Chart I) are to be considered to explain the dynamic process: the oxygen is trans to the allyl group in the conformer A, while it is cis to the allyl group in the other two. The conformers can interconvert via the mechanism of "trigonal twist".[13a] The conformers B and C constitute an enantiomeric pair, and therefore they will be of identical

(10) The needle-shaped crystals grown from aqueous $CH_3CN$ were not suitable for X-ray studies, since they were twins. After several trials, platelike crystals could be grown from toluene–hexane, which were used for the structure determination. A similar problem with pyrazolylborate complexes was reported earlier: Cotton, F. A.; Frenz, B. A.; Stanislowski, A. G. *Inorg. Chim. Acta* **1973**, *7*, 503.

(11) Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 155.

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(13) (a) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

energy and will be indistinguishable by NMR spectroscopy. From the structure of any one of these enantiomers, it can be seen that the two pyrazolyl groups and the terminal allyl protons have nonequivalent environments. At slow exchange rate, they would show distinct signals in the ratio 1:1. In all the three cases presented here, the ratio of the pair of signals is indeed 1:1. No signal is observed for the conformer A.

An EHMO calculation[14] was carried out to estimate the energy difference between the conformers A and B. The input structures were generated from the coordinates of the X-ray study and the subsequent trigonal twist of the three relevant donor ligands. The energy of the conformer A was found to be higher than that of B by 28 kcal/mol. Even if one prefers not to emphasize the magnitude of the energy difference, the preference of a non-pyrazole donor in such bis(pyrazolyl) chelates for a site cis to the π-allyl appears to be a general trend.[7,15-17] In this context it may be interesting to recall that in a number of five-membered chelates containing N or O donors[18] the chelating ligands occupy equatorial positions cis to the allyl group, while for 1,2-diphosphinoethanes one of the phosphorus atoms remains trans to the allyl group.[13a]

The reason for the difference in barrier height (trigonal twist) consequent to the different substitution at the 2-position of the allyl group is not immediately apparent,[12] but the trend is in agreement with earlier observations:[19] 2-methyl substitution has a lower barrier than 2-H or 2-Ph.

The origin of oxygen on the phosphorus atom can be explained in terms of an unexpected hydrolysis caused by traces of moisture in the reaction medium. The only other example of such in situ hydrolysis involves a pyrazolylgallate[15] ligand. In both instances, hydrolytic cleavage of one of the pyrazoles occurred during the ligand exchange prior to isolation. The presence of free pyrazole could be detected in the NMR spectrum of the crude product before workup, which showed that the hydrolysis occurred during the reaction and not during subsequent aqueous treatment.

An intriguing fact must be mentioned. With use of this ligand 1, a few sandwich (metal:ligand = 1:2) complexes were prepared in warm 50% aqueous acetonitrile from Co(II), Ni(II), and Cu(II) salts. With Cu(I), a 1:1 complex was formed. The spectral and microanalytical data confirmed the integrity of the ligand 1 in all these complexes,[20] demonstrating that the aqueous environment alone was not responsible for hydrolysis of the ligand in the case of molybdenum compounds. Attempts to prepare the desired molybdenum allyl complexes by rigorous exclusion of moisture have not been successful so far.

**Table IV. Crystallographic Data for Compound 4c**

| | |
|---|---|
| mol formula | $C_{21}H_{23}MoPO_4N_4$ |
| fw | 522.34 |
| space group | $P2_12_12_1$ |
| $a$, Å | 10.013 (1) |
| $b$, Å | 14.154 (2) |
| $c$, Å | 15.951 (2) |
| $V$, Å$^3$ | 2260.7 (5) |
| $\rho$(calcd), g cm$^{-3}$ | 1.53 |
| $Z$ | 4 |
| radiation (λ, Å) | Cu Kα (1.5418) |
| $F$(000) | 1063.8 |
| $\mu$, cm$^{-1}$ | 57.2 |
| $T$, K | 293 |
| scan range, deg | $0 < \theta < 60$ |
| no. of rflns | 1949 |
| no. of rflns with $I > 3\sigma(I)$ | 1842 |
| no. of variables | 280 |
| largest shift/esd | 0.08 |
| $R$ | 0.082 |

## Experimental Section

All reactions were performed under argon. No special precaution was necessary during the isolation of the complexes, since they were fairly air stable in the solid state and in solution for a brief period. Acetonitrile was distilled over $P_2O_5$ under argon directly into the reaction flask. 3,5-Dimethylpyrazole was prepared from hydrazine and acetylacetone. $Mo(CO)_6$ was purchased from Aldrich/Fluka, and $POCl_3$ and 2-methyllyl chloride were purchased from Fluka; all were used as received. Allyl chloride and allyl bromide (BDH) were distilled prior to use. 2-Phenyl-3-bromo-1-propene was prepared from α-methylstyrene[21] and freshly distilled before use.

The IR spectra were recorded on a Perkin-Elmer 599B instrument. The $^1$H NMR spectra were recorded on Bruker WH-90 and Varian 80A machines. The variable-temperature studies were carried out on Bruker WH-90 and MSL 300 spectrometers. The $^{13}$C spectra were recorded on a Bruker MSL 300 instrument operating at 75.5 MHz. For the solid state, chemical shifts are reported with reference to the methylene carbon resonance of adamantane at 37.8 ppm (external standard).

**Preparation of Tris(3,5-dimethyl-1-pyrazolyl)phosphine Oxide (1).** To a solution of 3,5-dimethylpyrazole (12.66 g, 132 mmol) and triethylamine (18.15 g, 180 mmol) in benzene (125 mL), maintained at 0–5 °C, was added $POCl_3$ (8.2 g, 53.5 mmol) in benzene (25 mL) dropwise over a period of 30 min with stirring. The reaction mixture was stirred for 1 h at room temperature and then heated under reflux for 10 h (monitored by TLC). After the mixture was cooled to room temperature, it was filtered and the residue was washed with dry benzene. Benzene was evaporated on a rotary evaporator. The colorless sticky residue was dissolved in $CCl_4$ (9 mL), and to this solution was added petroleum ether (50 mL). The turbid solution was kept in a refrigerator for 15 days to furnish white crystals of compound 1 (8.5 g, 59%), mp 105 °C (lit.[8] mp 105–108 °C). The crystals were hygroscopic and best preserved under petroleum ether.

**Preparation of (Tris(3,5-dimethyl-1-pyrazolyl)phosphine oxide)tricarbonylmolybdenum(0) (2).** A suspension of $Mo(CO)_6$ (2 g, 7.56 mmol) in acetonitrile (50 mL) containing 1 (3.6 g, 10.84 mmol) was refluxed for 2 h. When the mixture was cooled to room temperature, the compound 2 was obtained as a yellow crystalline precipitate (2.24 g, 58%).

**Preparation of 4a.** A mixture of $Mo(CO)_6$ (1 g, 3.78 mmol) and allyl chloride (2 mL) in acetonitrile (15 mL) was heated under reflux for 5 h. After the mixture was cooled to room temperature, a solution of the ligand 1 (1.3 g, 3.9 mmol) in acetonitrile (5 mL) was added with a syringe. The reaction mixture was again heated for 15 min, cooled, and poured into water (100 mL). The yellow precipitate was collected by filtration and dried under vacuum (0.882 g, 52%). Analytically pure crystals of 4a were obtained

(14) (a) We are grateful to Professor Roald Hoffmann for providing us a copy of his ICON program (HP version). Calculations were done with the weighted $H_{ij}$ option, and parameters for Mo and P were taken from refs 12 and 13b. (b) The X-ray coordinates were typed into the IRIS graphics system to generate the structure file. A trigonal twist was simulated by generating torsion about an axis passing through the molybdenum and the centroid of the triangle defined by the two N atoms and one O atom around the metal. Fortunately, the axis was found to be perpendicular to the plane, and therefore, no distortion resulted from such a torsion. The distances between the atoms (Mo, N, N, and O) remained unchanged.

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by crystallization from aqueous acetonitrile. After prolonged storage at room temperature, the surface of the crystals turned brown, though NMR spectroscopy showed no perceptible decomposition. The same product **4a** was obtained when allyl bromide was used instead of allyl chloride.

**Preparation of 4b.** After $Mo(CO)_6$ (1 g, 3.78 mmol) was refluxed with 2-methallyl chloride (1 mL) in acetonitrile (15 mL) for 5 h, the ligand **1** (1.3 g, 3.9 mmol) in acetonitrile (5 mL) was added to the hot solution. The yellow crystalline product **4b** was isolated (0.77 g, 44%) as described for **4a**.

**Preparation of 4c.** The procedure is the same as that described for **4a**. From $Mo(CO)_6$ (1 g, 3.78 mmol), 2-phenyl-3-bromo-1-propene (0.75 mL), and ligand **1** (1.3 g, 3.9 mmol), there was obtained 0.436 g (23%) of **4c** as a yellow solid.

**Attempted Preparation of 4c from 2.** The complex **2** (0.25 g, 0.49 mmol) was refluxed with allyl bromide (1 mL) in acetonitrile (20 mL) containing THF (3 mL) for 4 h. No change was observed by TLC. When the mixture was cooled, the complex **2** (0.2 g) was recovered.

**X-ray Crystal Structure Determination of 4c.** An X-ray-grade crystal of **4c** was grown in toluene–hexane. Diffraction data were collected for a crystal of size 0.275 × 0.45 × 0.5 mm on an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions were determined with use of 25 well-centered reflections located in the region $17° < \theta < 41°$. An orthorhombic cell was indicated with cell constants as listed in Table IV. Reflections were measured with an index range $h = 0$–11, $k = 0$–15, and $l = 0$–17 with use of the $\omega/2\theta$ scan mode and an average scan speed of 1° $min^{-1}$. Three standard reflections monitored every 3000 s of X-ray time showed negligible variation in intensity.

From the systematically absent reflections in the data set, the space group $P2_12_12_1$ was inferred. The structure was solved with use of Patterson and Fourier techniques. Refinement of the structure with use of SHELX-76[22] converged to $R = 0.0817$ for 1842 observed reflections. A weighting scheme was not applied. Non-hydrogen atoms were treated with anisotropic temperature factors. Hydrogens that could be geometrically fixed were held constant during the last few cycles of refinement.

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**Supplementary Material Available:** Tables of bond lengths and bond angles and atomic coordinates and a crystal packing diagram for **4c** (5 pages); a table of structure factor amplitudes for **4c** (11 pages). Ordering information is given on any current masthead page.

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# Reduction of Molybdenum Imido–Alkylidene Complexes in the Presence of Olefins To Give Molybdenum(IV) Complexes

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$Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ (**1a**) (Ar = 2,6-diisopropylphenyl) reacts with excess vinyltrimethylsilane to give $Mo(NAr)[OCMe(CF_3)_2]_2(CH_2{=}CHSiMe_3)$ (**2**). Complex **2** reacts with trimethylphosphine, 2-butyne, and excess ethylene to give $Mo(NAr)[OCMe(CF_3)_2]_2(PMe_3)_2$ (**3**), $Mo(NAr)[OCMe(CF_3)_2]_2(MeC{\equiv}CMe)$ (**4**), or $Mo(NAr)[OCMe(CF_3)_2]_2(C_4H_8)$ (**8**), respectively. Complex **4** reacts with $PMe_3$ to give $Mo(NAr)[OCMe(CF_3)_2]_2(MeC{\equiv}CMe)(PMe_3)$ (**5**), and **8** reacts with $PMe_3$ to give $Mo(NAr)[OCMe(CF_3)_2]_2(CH_2{=}CH_2)(PMe_3)$ (**9**). Metallacycle $Mo(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ (**6**) decomposes in the presence of excess ethylene to form **8** and reacts with trimethylphosphine to give $Mo(CH_2)(NAr)[OCMe(CF_3)_2]_2(PMe_3)$ (**7**). $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (**1b**) reacts with excess ethylene to give $Mo(CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$ (**10**), which reacts with trimethylphosphine to give $Mo(CH_2)(NAr)(O\text{-}t\text{-}Bu)_2(PMe_3)$ (**11**). **10** decomposes to $[Mo(NAr)(O\text{-}t\text{-}Bu)_2]_2$ (**12**; $C2/c$, $a = 14.772$ (6) Å, $b = 15.470$ (4) Å, $c = 10.625$ (8) Å, $\beta = 104.62$ (3)°, $Z = 4$, $M_r = 834.88$, $\rho = 1.276$ g/cm$^3$, $\mu = 5.99$ cm$^{-1}$, $R_1 = 0.035$, $R_2 = 0.047$). **12** is an imido-bridged dimer that is believed to form upon coupling of methylene ligands in two $Mo(NAr)(CH_2)(O\text{-}t\text{-}Bu)_2$ complexes.

## Introduction

Complexes of the type $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ (M = Mo,[1] W;[2] Ar = 2,6-diisopropylphenyl; R = alkyl, aryl, fluoroalkyl) have proven to be useful olefin metathesis catalysts. When R is relatively electron withdrawing (i.e., R = $CMe(CF_3)_2$), they will metathesize acyclic olefins. When R is relatively electron donating (i.e., R = *t*-Bu), they do not react readily with acyclic olefins but do react rapidly with strained cyclic olefins, especially norbornenes and norbornadienes.[3] Molybdenum complexes appear to be more tolerant of functionalities than tungsten complexes,[4] but they also appear to be less stable than their tungsten analogues.[1] In particular, molybdenum olefin metathesis catalysts appear to decompose more readily by pathways that yield reduced (Mo(IV)) complexes.[1] In this paper we attempt to clarify these decomposition pathways and the

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