C–C Coupling between an η^3-Allyl Ligand and Carbon Nucleophiles in Molybdenum and Tungsten Complexes: Structural Characterization of the Key Intermediate**

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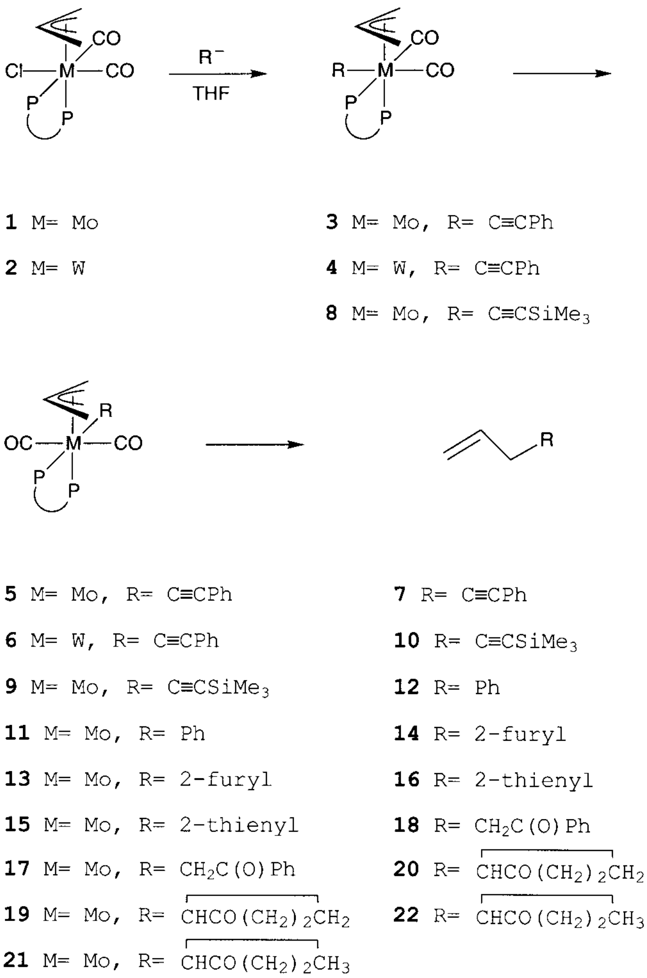
The Mo-catalyzed allylic alkylation was first reported by Trost and Lautens in 1982[1] and has been developed into a useful tool in organic synthesis.[2] It is accepted that in this reaction the oxidative addition of the allylic electrophile to a low-valent molybdenum carbonyl complex gives a η^3-allyl complex, which subsequently undergoes attack by the nucleophile.[3] Accordingly, $[MoCl(\eta^3\text{-allyl})(CO)_2(L{-}L)]$ (L–L = 2,2′-bipyridine (bpy) or 1,2-bis(diphenylphosphanyl)ethane (dppe)) complexes react with stabilized carbanions to afford olefins.[1, 4] Despite studies on this reaction[3] and the related W-catalyzed allylic alkylation,[5] some important mechanistic questions remain open. Thus, as stated in the seminal paper by Trost and Lautens,[1] nucleophilic attack can take place either directly at the allyl group or primarily at the metal center, followed by a metal-to-allyl migration of the alkyl group.

We recently found that $[MoCl(\eta^3\text{-allyl})(CO)_2(N{-}N)]$ complexes react with nonstabilized alkyl nucleophiles to yield $[Mo(R)(\eta^3\text{-allyl})(CO)_2(N{-}N)]$ alkyl complexes.[6] In these complexes, whose geometry is reminiscent of that of the chloro precursors,[7] the alkyl and allyl groups are in mutually *trans* positions and, as a result, alkyl migration to the allyl ligand was not observed.

$[MoCl(\eta^3\text{-allyl})(CO)_2(P{-}P)]$ diphosphane complexes have a different structure, in which the Cl and allyl ligands are in *cis* positions.[8] We reasoned that substitution of Cl^- by R^- with retention of the geometry in these diphosphane complexes, as in the diimine counterparts, would afford products in which coupling between the adjacent R and allyl groups could be viable. To begin our study, we chose acetylide anions because alkynyl complexes are more stable than their alkyl counterparts.[9]

Preliminary experiments with bis(diphenylphosphanyl)methane (dppm) and dppe complexes afforded products from which we were unable to isolate pure samples, whereas the related $[MCl(\eta^3\text{-}C_3H_5)(CO)_2(dmpm)]$ (M = Mo (**1**), W (**2**), dmpm = (dimethylphosphanyl)) compounds led to more tractable products and the reactivity of these complexes is described herein.

The reactions of **1** and **2** with lithium phenylacetylide gave metal species with two similarly intense ν_{CO} bands at wavenumbers lower than for **1** and **2**, as expected for the substitution of Cl for $C\equiv CPh$. These compounds (**3** and **4**), for which the *cis* geometry depicted in Scheme 1 can be assumed, could not be further characterized because of their rapid transformation into the new complexes **5** and **6**, respectively, which displayed single ν_{CO} IR bands. These complexes decomposed in solution; however, in the case of **6** this decomposition was slow enough to permit a full characterization (see Experimental Section) in solution and the crystallization and subsequent structural determination by X-ray diffraction (Figure 1).[10]



Scheme 1. Reactions of **1** and **2** with acetylide, alkyl, and enolate carbanions.

Compound **6** comprises a tungsten atom coordinated to a chelating dmpm ligand, a η^3-allyl group, a phenylalkynyl ligand, and two carbonyl groups. The CO ligands are in mutually *trans* positions,[12] an arrangement that is considered to be electronically disfavored, and unprecedented for pseudooctahedral allylmolybdenum dicarbonyl complexes.[7]

The solutions obtained from the decomposition of complexes **5** and **6** (disappearance of ν_{CO} IR bands, and the

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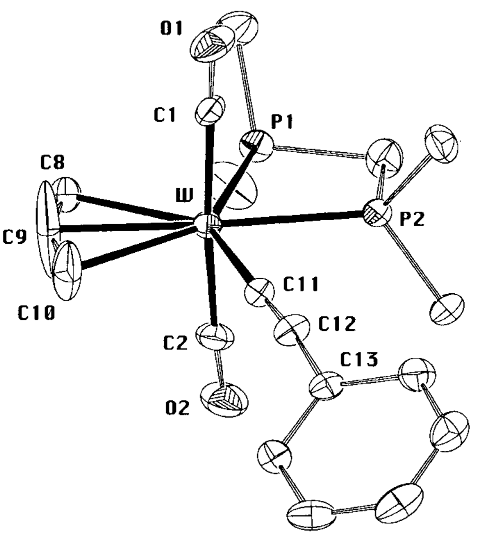

Figure 1. Structure of **6** (thermal ellipsoid plot (30% probability)). Selected bond lengths [Å] and angles [°]: W-C11 2.177(9), C11-C12 1.192(11), C12-C13 1.430(11); C1-W-C2 175.2(3), C11-C12-C13 172.6(9).

observation of a large number of ^{31}P MNR signals in the resulting solution showed the decomposition of the metal complex to several unidentified species) contained the non-conjugate enyne 1-phenyl-4-penten-1-yne (**7**), which resulted from the coupling between the alkynyl group and a terminal carbon atom of the allyl group. Monitoring of the reaction by ^{1}H NMR spectroscopy in CD_2Cl_2 revealed quantitative formation of the enyne from **5** and **6**. Since η^3-allyl complexes[13] are normally the target of nucleophilic attack, and alkynyl groups typically react with electrophiles, enyne formation can be pressumed to occur by an alkynyl-to-allyl intramolecular migration.[14] Analogous results were obtained by employing lithium trimethylsilylacetylide (see Scheme 1; **9**→**10**).

The reaction of the **1** with phenyl- (via **11** to give **12**), 2-furyl- (via **13** to give **14**), and 2-thienyllithium reagents (via **15** to give **16**) followed a similar path. Only the *trans*-dicarbonyl complexes were detected by IR spectroscopy, probably as a result of a fast *cis*-to-*trans* isomerization. Decomposition of the metal complexes afforded the olefins resulting from alkyl–allyl coupling (Scheme 1). Similar results were obtained with the enolates of acetophenone, cyclopentanone, and cyclohexanone, which afforded the C–C coupled products **18**, **20**, and **22**, respectively (see Scheme 1).

These results demonstrate that acetylide, alkyl, and enolate carbanions attack at the metal center in $[MCl(\eta^3\text{-}C_3H_5)(CO)_2(dmpm)]$ (M = Mo (**1**), W (**2**)) complexes, leading to a stereospecific substitution of the chloro ligand by the incoming nucleophile. The products then undergo a *cis*-to-*trans* isomerization, which is unprecedented for this kind of complexes, and, subsequently, the spontaneous elimination of the alkynyl–allyl, alkyl–allyl, or enolate–allyl product. Nucleophilic attack at the metal center followed by a metal-to-allyl migration, which was proposed as a possible mechanistic path two decades ago for pseudooctahedral allylmolybdenum complexes,[1] has been, therefore, experimentally substantiated for the first time.

Experimental Section

All operations were carried out under an atmosphere of dry dinitrogen by using Schlenk techniques. Solvents were dried over Na (hexane) and CaH_2 (CH_2Cl_2 and MeOH) and distilled immediately prior to use. IR spectra were recorded in solution in THF. Correct elemental analyses were obtained for the new complexes.

1: The addition of dmpm (50 µL, 0.32 mmol) to $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$[15] (0.10 g, 0.32 mmol) in CH_2Cl_2 (10 mL) gave a red solution which was stirred for 5 min. The volume of this solution was reduced under vacuum to one third, and hexane was added to precipitate **1** as an orange crystalline solid. Yield: 0.11 g, 94%; IR: $\tilde{\nu} = 1944$ s, 1845 s cm^{-1}; ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta = -24.38$; ^{1}H NMR (CD_2Cl_2): $\delta = 4.75$ (m, 1H; Hc), 3.69 (m, 2H; *syn*-H), 3.24 (m, 2H; CH_2 (dmpm)), 2.31 (d, ^3J(H,H) = 12 Hz, 2H; *anti*-H), 1.73 (apparent triplet (at), ^2J(P,H) = 5 Hz, 6H; CH_3 (dmpm)), 1.65 (at, ^2J(P,H) = 5 Hz, 6H; CH_3 (dmpm)); ^{13}C{^{1}H} NMR (CD_2Cl_2): 226.68 (at, ^2J(P,C) = 8 Hz; CO), 98.68 (s; C_2 allyl), 62.36 (s; C1 and C3 (allyl)), 40.65 (at, ^1J(P,C) = 23 Hz; CH_2 (dmpm)), 17.34 (at, ^1J(P,C) = 14 Hz; CH_3 (dmpm)), 13.40 (at, ^1J(P,C) = 13 Hz; CH_3 (dmpm)).

5: LiC≡CPh (0.27 mmol in THF (5 mL)) was added to a solution of **1** (0.10 g, 0.27 mmol) in THF (20 mL) at −78°C. The red color darkened immediately and the IR spectrum showed bands at 2072 w, 1935 s, and 1820 s cm^{-1}, which were assigned to **3**. After stirring (40 min, RT, transformation to **5** was monitored by IR spectroscopy), solvent evaporation, extraction (CH_2Cl_2, 5 mL), filtration (alumina, grade IV), and evaporation, **5** was obtained. Yield: 0.09 g, 68.1%; IR: $\tilde{\nu} = 2074$ w, 1852 s cm^{-1}; ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta = -8.85$, -20.04 (ABq, ^2J(P,P) = 81 Hz); ^{1}H NMR (CD_2Cl_2): $\delta = 7.28-7.15$ (m, 5H; Ph), 5.25 (m, 1H; Hc), 3.19 (m, 2H; CH_2 (dmpm)), 3.05 (m, 2H; *syn*-H); 2.93 (d, ^{3}J(H,H) = 9 Hz, 1H; *anti*-H), 2.06 (dd, ^3J(H,H) = 11 Hz, ^3J(H,H) = 3 Hz, 1H; *anti*-H), 1.93 (d, ^2J(P,H) = 10 Hz, 3H; CH_3 (dmpm)), 1.74 (at, ^2J(P,H) = 10 Hz, 3H; CH_3 (dmpm)), 1.70 (d, ^2J(P,H) = 9 Hz, 3H; CH_3 (dmpm)), 1.53 (d, ^2J(P,H) = 9 Hz, 3H; CH_3 (dmpm)). Compound **5** decomposed in solution in 2 h to give a quantitative (^{1}H NMR) amount of 1-phenyl-4-penten-1-yne (**7**).[14]

11, **13**, **15**, **18**, **20**, **22:** PhLi (0.13 mL of a 1.8 M solution, 0.23 mmol) was added to a solution of **1** (0.10 g, 0.23 mmol) in THF (20 mL). After 10 min, the IR spectrum showed a single ν_{CO} band at 1841 cm^{-1}, which was assigned to **11**. After 2 h at room temperature, a procedure analogous to that for **5** afforded allylbenzene (**12**).

Similar reactions were conducted with Li (alkyl) or K (enolate) reagents to give the products indicated in Scheme 1. Available data for the *trans*-dicarbonyl complexes, reaction times, and references for the non-commercial coupling products are given: **11:** IR: $\tilde{\nu} = 1841$ s cm^{-1}, 2 h; **12**: commercial; **13**: $\tilde{\nu} = 1840$ s cm^{-1}, ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = -4.72$, -18.79 (ABq, ^2J(P,P) = 69.5 Hz), 30 min; **14**:[16]; **15**: $\tilde{\nu} = 1845$ s cm^{-1}, 40 min; **16:**[17]; **17**: $\tilde{\nu} = 1840$ s, 1689 s cm^{-1}, ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 67.27$, 11.73 (ABq, ^2J(P,P) = 26.8 Hz), 2 h; **18**:[18]; **19**: $\tilde{\nu} = 1847$ s, 1784 s cm^{-1}, 4 h; **20**:[19]; **21**: $\tilde{\nu} = 1843$ s, 1785 s cm^{-1}, 4 h; **22**: commercial. Experimental details for **2**, **6**, and **9** are in the Supporting Information.

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[10] X-ray structure analysis of **6**: Crystal grown from CH_2Cl_2/hexane; crystal dimensions $0.33 \times 0.33 \times 0.10$ mm^3; $C_{18}H_{24}O_2P_2W$ (M_r = 518.16); monoclinic, space group $P2_1/c$, $a = 9.256(2)$, $b = 12.571(2)$, $c = 17.942(6)$ Å, $\beta = 103.15(4)^\circ$, $V = 2032.9(9)$ Å^3, $Z = 4$, ρ = 1.693 Mg m^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 5.845$ mm^{-1}, $\lambda = 0.71073$ Å ($\mathrm{Mo}_{K\alpha}$ radiation, Nonius CAD4 single crystal diffractometer). Data collection at 293(2) K, ω-2θ scans, $2.0 < \theta < 25.97$. A total of 3984 unique reflections were collected, of which 2645 were observed with $I > 2\sigma(I)$. Crystal structure was solved by direct methods (SHELXS-97).[11a] An anisotropic least-squares refinement was carried out with SHELXL-97.[11b] The final cycle of full-matrix least-squares refinement based on 3984 reflections and 213 parameters converged to a final value of $R1$ ($F^2 > 2\sigma(F^2)$) = 0.0405, w$R2$ ($F^2 > 2\sigma(F^2)$) = 0.1071. Residual electron density 0.76/ − 1.30 e Å^{-3}. CCDC-1777731 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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The Stable Pentamethylcyclopentadienyl Cation**

Joseph B. Lambert,* Lijun Lin, and Vitaly Rassolov

The cyclopentadienyl anion, $C_5H_5^-$ (**1**, Cp^-), was first prepared one hundred years ago.[1] In due course it became a classic example of aromaticity, exemplifying the Hückel $4n+2$ rule for π electrons, along with benzene (**2**) and the tropylium cation (**3**).[2–4] In contrast, the cyclopentadienyl cation, $C_5H_5^+$ (**4**, Cp^+) has languished experimentally as an elusive charge variant. It shares with cyclobutadiene[5–7] (**5**) and the cycloheptatrienyl anion[8] (**6**), among others, the characteristics of possessing $4n$ π electrons and thus potentially being antiaromatic.


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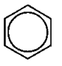
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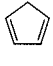
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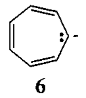
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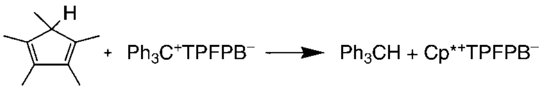
No simple cyclopentadienyl cation has been structurally characterized. Several studies have reported electron spin resonance (ESR) spectra,[9] and some studies have implied the species as an intermediate.[10] These investigations variously looked at the pentachloro, pentaphenyl, and pentamethyl derivatives as well as the unsubstituted molecule. In general, the observed cations were relatively unstable, possessed triplet multiplicity, and needed protective environment.

We now report the preparation of the pentamethylcyclopentadienyl cation $C_5Me_5^+$ (Cp^{*+}) as the tetrakis(pentafluorophenyl)borate ($TPFPB^-$) salt. The crystalline material obtained is stable for weeks at room temperature and can be left exposed to the open atmosphere without serious decomposition. We have solved the X-ray structure and obtained NMR spectra in the solid state and in solution. This material may be obtained in one step at room temperature by hydride abstraction from commercially available pentamethylcyclopentadiene [Eq. (1)].[11, 12] The trityl cation (Ph_3C^+, with the anion $TPFPB^-$) is converted into triphenylmethane, whereas pentamethylcyclopentadiene is converted into the corresponding cation. Crystals of the product began forming immediately and spontaneously. The overall yield is nearly quantitative, and yields of crystals have reached 40%. The reaction has been carried out in several solvents (benzene, toluene, dichloromethane) and with alternative (silyl) leaving groups.



(1)

The remarkable stability of this material may be attributed to a number of factors. First, the methyl groups clearly are critical, as analogous experiments with the unsubstituted system were unsuccessful. The methyl group serves as an electron donor and also may play a steric role, as described subsequently. The second key factor is the choice of the counteranion. Many anions of low nucleophilicity now are available.[13] We previously utilized $TPFPB^-$ in the preparation of the first silylium cation[14] and employ this same anion in the present study. Finally, choice of solvent also is critical, as

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