Platinum−Molybdenum Complexes of Cyclic Tropynes, Cumulenes, and Alkynes

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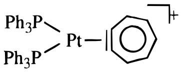
The bis(triphenylphosphine)platinum complexes of tropyne (**1**), cyclohepta-3,5-dien-1-yne (**12**), and cyclohepta-1,5-dien-3-yne (**13**) react rapidly with (η^6-*p*-xylene)Mo(CO)$_3$ in a mixture of CD_2Cl_2 and THF-d_8 to give the bimetallic complexes **4**−**6**. Reduction of **4** with LiAl(O-*t*-Bu)$_3$H or KBEt$_3$H gives a mixture of **5**−**7** (essentially quantitative) in a ratio of 5:10:85 and 8:21:71, respectively. The major isomer contains a 1,2,3,5-cycloheptatetraene ring, a ring system that has previously been inaccessible either free or complexed to a transition metal. Hydride abstraction from **5**, **6**, or **7** regenerates **4**. X-ray crystal structures for **5** and **7** are reported. The absolute configuration of complex **7** in the crystal was determined.

Introduction

In contrast to benzyne[1] and its transition metal complexes,[2] which have been studied extensively, to date published information about tropyne, benzyne's next higher homologue, has been limited to platinum[3] (**1**) and zirconium[4] (**2**) complexes of the parent and one



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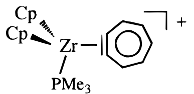

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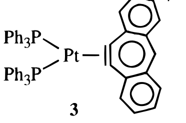

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platinum complex of a dibenzannelated analog (**3**).[5] As a continuation of our work on the chemistry of **1**, and its cycloheptadienyne precursors **12** and **13**, we have now prepared their Mo(CO)$_3$ bimetallic complexes (**4**−**6**) and have made the surprising discovery that reduction of the tropyne complex gives a good yield of a new C_7H_6 ring system.

Results and Discussion

Preparation of 4 by Tropyne−Arene Exchange. It has been found[6] that reaction of [Mo(η^7-C$_7$H$_7$)(η^6-C$_6$H$_6$)]$^+$ with nucleophilic ligands leads to displacement of benzene leaving the tropylium ligand intact. This suggests that the tropylium ion may be bonded to molybdenum more strongly than arenes. Since tropyne can be regarded as a substituted tropylium ion and since the aromatic ring can be readily displaced[7] in (η^6-arene)-Mo(CO)$_3$ by more basic arenes, it occurred to us that it might be possible to use an arene exchange reaction to attach the Mo(CO)$_3$ fragment to the tropyne ring in **1**. Indeed, reaction of the tropyne complex **1** with 1 equiv of (η^6-*p*-xylene)Mo(CO)$_3$ at room temperature in a mixture of CD_2Cl_2 and THF-d_8 led to an essentially instantaneous color change from red to brown-red. Comparison of the NMR spectra of this solution with the tropyne complex synthesized more conveniently by hydride abstraction from a mixture of **5** and **6** (vide infra) confirmed the essentially quantitative yield of **4** (Scheme 1). Unfortunately, we were unable to grow crystals of this red-brown solid that were suitable for X-ray diffraction. However, the bimetallic complex was completely characterized by multinuclear NMR spectroscopy, IR, and HRMS. In the ^{1}H NMR, in addition to PPh$_3$ signals three different resonances are displayed in the range δ 5.55−6.1 ppm with the one at δ 5.55 ppm showing coupling to the ^{195}Pt nucleus. The multiplicity of these three signals is the same as that of **1** but each is shifted ca. 3 ppm upfield from **1**. Both the ^{19}F{^{1}H} and the ^{31}P{^{1}H} NMR show singlets whereas the ^{195}Pt-{^{1}H} NMR exhibits a triplet centered at δ −4087.6 ppm. The chemical shift of the ^{195}Pt nucleus is 308 ppm upfield from the corresponding resonance for complex **1**. The IR spectrum displays two very strong bands (2036, 1976 cm^{-1}) in the metal carbonyl region. These stretching frequencies are ca. 40 cm^{-1} lower than those of the Mo(CO)$_3$ complex of the tropylium cation which is consistent with a somewhat more electron-rich tropyne ring in the former [from electron donation from bis(triphenylphosphine)platinum]. The carbonyl region in the ^{13}C NMR shows only one peak, even at −100 °C, indicating a very low barrier for rotation of the molybdenum tricarbonyl around the molybdenum−seven-membered-ring axis.

Hydride Reduction of (PPh$_3$)$_2$Pt{η^2[(η^7-C$_7$H$_5$)Mo(CO)$_3$]} (4). Reduction of **4** with either KBEt$_3$H or LiAl(O-*t*-Bu)$_3$H was noticeably cleaner (as shown by the ^{31}P NMR) than the corresponding reactions with **1** or **2**, giving a mixture in which **7** is the major product (**5**:**6**:**7** = 5:10:85 for LiAl(Ot-Bu)$_3$H and 8:21:71 for KBEt$_3$H) (Scheme 2). Selective formation of **7** from hydride addition to the tropyne carbon indicated by arrow b was not only unexpected but was of particular interest because the resulting 1,2,3,5-cycloheptatetraene ring in

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(1) Hoffmann, R. Q. *Dehydrobenzene and Cycloalkynes*; Verlag Chemie: Weinheim, Germany, 1967.

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(3) Lu, Z.; Abboud, K. A.; Jones, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10991.

(4) Lu, Z.; Jones, W. M. *Organometallics* **1994**, *13*, 1539.

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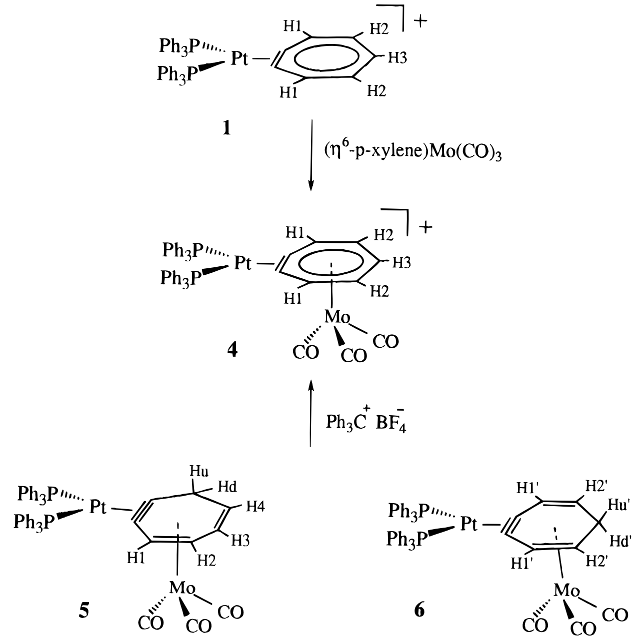
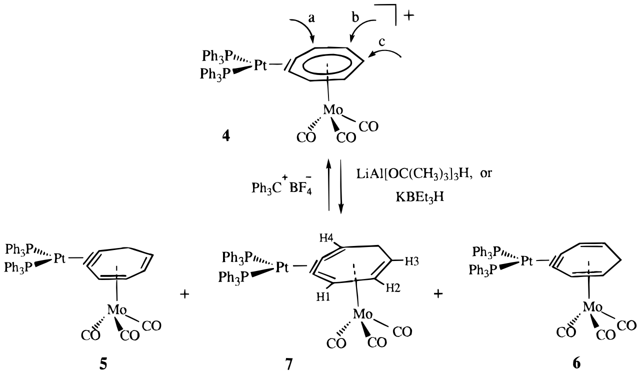
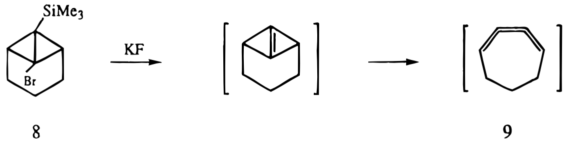
Scheme 1



Scheme 2



7 has not been previously reported; to date the only recorded butatriene confined to a seven-membered ring is **9**,[8] which was prepared by desilabromination of **8** with KF followed by isomerization.



Attempts to prepare a platinum complex of 1,2,3,5-cycloheptatetraene (**11**) by β-elimination had yielded only **12**,[9] **13**,[9] and **14**[10] (Scheme 3).

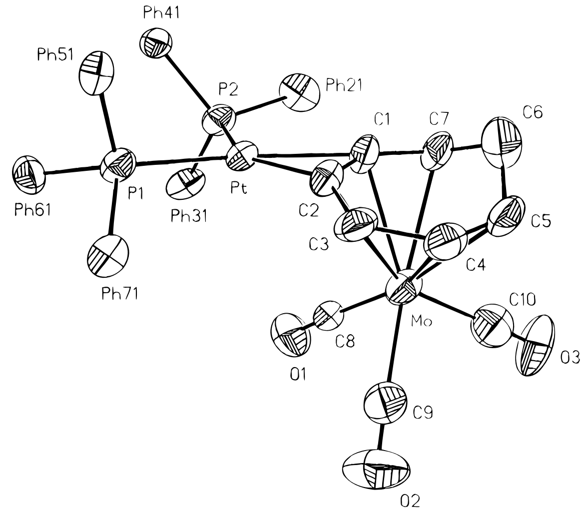
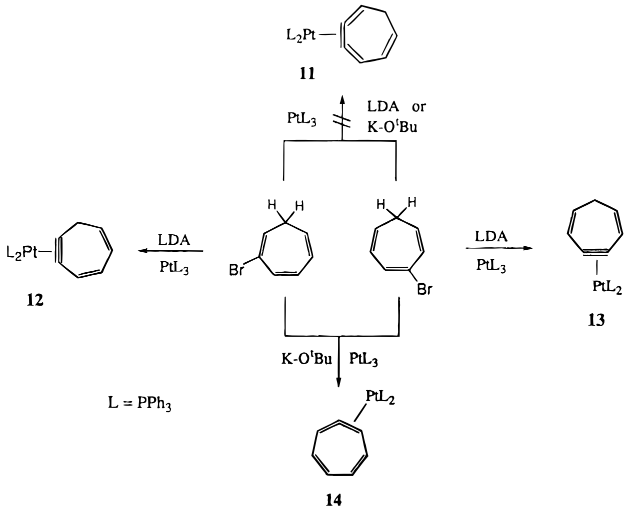


Figure 1. Structure and labeling scheme for **7** with 40% probability of thermal ellipsoids. Triphenylphosphine phenyl rings are omitted for clarity.

Scheme 3



The cumulene complex crystallized from the reaction mixture to give red crystals in 42% yield. Its ^{1}H NMR showed six different resonances with two showing coupling to the ^{195}Pt nucleus. One of these signals (at δ 3.85) showed coupling to one of the methylene protons and was therefore assigned to H4. Consequently the other signal coupled to ^{195}Pt at δ 5.84 was assigned to H1. The remaining signals in the spectrum were assigned on the basis of a 2D COSY experiment. The ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR appeared as doublets of doublets centered at δ −4420.2 (dd, $^1J_{\mathrm{Pt-P'}} = 3124$ Hz, $^1J_{\mathrm{Pt-P''}} = 3282.5$ Hz) and a pair of doublets at δ 23.81, 23.55 (d, $^2J_{\mathrm{P'-P''}} = 9.2$ Hz), respectively, which is consistent with the C1 symmetry for **7**. The ^{13}C{^{1}H} NMR exhibited a broad singlet in the carbonyl region which decoalesced at −35 °C to three resonances of equal intensity. This observation indicates that the molecule is fluxional and that the origin of this process is a rapid spinning of the Mo(CO)$_3$ fragment around the metal–seven-membered-ring axis. The IR spectrum showed three very strong peaks in the carbonyl region with stretching frequencies (1947, 1870.8, 1847 cm^{-1}) lower than **15** (1970, 1908, 1856 cm^{-1})[11] and interestingly even lower (ca. 10 cm^{-1}) then **5** (see below). The structure of **7** was further confirmed by hydride abstraction to regenerate **4** and by an X-ray diffraction study. The two minor reduction products **5** and **6** which were formed as a result of hydride addition to the tropyne carbons indicated by arrows a (**5**) and c (**6**)

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[10] Winchester, W. R.; Gawron, M.; Palenik, G. J.; Jones, W. M. *Organometallics* **1985**, *4*, 1894.

[11] The IR spectrum of (C$_7$H$_8$)Mo(CO)$_3$ was measured in our laboratory under the same condition as those of other complexes.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 7

Pt−P1	2.287(5)	Pt−P2	2.293(6)
Pt−C1	2.084(13)	Pt−C2	2.01(2)
P1−C51	1.80(2)	P1−C61	1.84(2)
P1−C71	1.84(2)	P2−C21	1.81(2)
P2−C31	1.75(2)	P2−C41	1.82(2)
Mo−C1	2.36(2)	Mo−C2	2.38(2)
Mo−C3	2.33(2)	Mo−C4	2.40(3)
Mo−C5	2.45(2)	Mo−C7	2.50(2)
Mo−C8	1.98(2)	Mo−C9	2.03(3)
Mo−C10	2.05(3)	C1−C2	1.30(3)
C1−C7	1.33(2)	C2−C3	1.39(3)
C3−C4	1.42(3)	C4−C5	1.28(4)
C5−C6	1.58(4)	C6−C7	1.52(3)
P1−Pt−P2	106.7(2)	P1−Pt−C1	141.3(8)
P2−Pt−C1	111.0(7)	P2−Pt−C2	148.0(5)
C1−Pt−C2	37.0(9)	C2−Pt−P1	105.0(5)
C2−C1−C7	139.(2)	C2−C1−Pt	68.4(9)
C3−C2−Pt	152.(2)	C3−C2−C1	130.(2)
C4−C3−C2	125.(2)	C5−C4−C3	125.(3)
C6−C5−C4	128.(2)	C7−C6−C5	115.(2)
C1−C7−C6	110.(2)	Mo−C8−O1	176.(2)
Mo−C9−O2	178.(2)	Mo−C10−O3	179.(2)

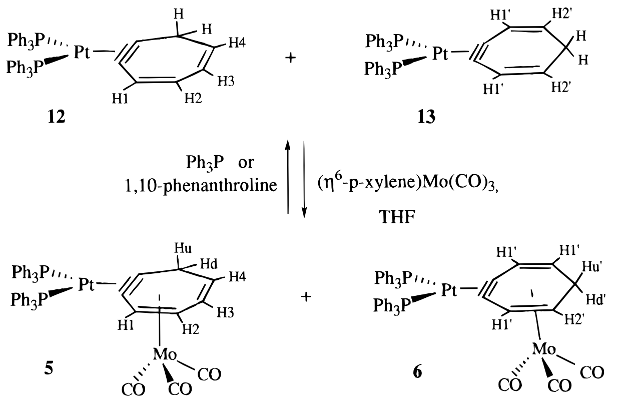
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 5

Pt−P1	2.275(2)	Pt−P2	2.297(2)
Pt−C1	2.033(10)	Pt−C2	2.025(10)
P1−C51	1.818(9)	P1−C61	1.836(8)
P1−C71	1.826(8)	P2−C21	1.829(9)
P2−C31	1.824(90	P2−C41	1.847(9)
Mo−C1	2.453(10)	Mo−C2	2.364(9)
Mo−C3	2.379(10)	Mo−C4	2.359(13)
Mo−C5	2.35(2)	Mo−C6	2.466(14)
Mo−C8	1.950(14)	Mo−C9	1.945(12)
Mo−C10	2.008(11)	C1−C2	1.292(14)
C1−C7	1.524(15)	C2−C3	1.422(14)
C3−C4	1.39(2)	C4−C5	1.40(2)
C5−C6	1.36(3)	C6−C7	1.50(2)
P1−Pt−P2	102.42(8)	P1−Pt−C1	143.2(3)
P2−Pt−C1	114.4(3)	P2−Pt−C2	151.2(3)
C1−Pt−C2	37.1(4)	C2−Pt−P1	106.2(3)
C2−C1−C7	133.9(11)	C2−C1−Pt	71.1(6)
C3−C2−Pt	152.0(8)	C3−C2−C1	134.2(10)
C4−C3−C2	121.6(11)	C5−C4−C3	127.1(14)
C6−C5−C4	134.(2)	C7−C6−C5	129.7(14)
C1−C7−C6	107.8(10)	Mo−C8−O1	177.1(10)
Mo−C9−C2	175.7(11)	Mo−C10−C3	176.9(8)

(Scheme 2) were identified by comparison with authentic samples synthesized as described below.

Crystal Structure of $(PPh_3)_2Pt[\eta^2(\eta^6\text{-}C_7H_6)Mo(CO)_3]$ (7). Suitable crystals for X-ray diffraction analysis were obtained from a mixture of benzene and hexane at −16 °C. A thermal ellipsoid drawing of **7** is presented in Figure 1, while crystal data are included in Table 3. Selected bond distances and angles and final fractional atomic coordinates are provided in Tables 1 and 4, respectively. Complex **7** crystallized in monoclinic, noncentrosymmetric space group $P2_1$ with one molecule of benzene located in the general position. Complex **7** is chiral, and since it crystallized in a noncentrosymmetric space group, only one enantiomer can be present in the crystal. By refining both enantiomers with the same data set and comparing the refinement results, we were able to determine the absolute configuration of the complex in the crystal (for more information see the Experimental Section). The geometry around the Pt atom is square planar. The platinum atom is bonded to two phosphorus and two carbon atoms. Six carbon atoms belonging to the seven-membered ring are coplanar (maximum deviation from the least-squares plane is 0.08(3) Å for C3) whereas C6 is 0.68(3) Å above this plane. The dihedral angle between the planes defined by C7−C6−C5 and C7−C1−C2−C3−C4−C5 is equal to 127(2) °C. This value is in the normal range for molybdenum cycloheptatriene complexes.[12] A bond length analysis could not be made due to low data quality. Unfortunately all attempts to get better data sets were unsuccessful.

Scheme 4



Preparation of 5 and 6 by Arene Exchange. Complexes **12** and **13** can be viewed as substituted cycloheptatrienes, and since cycloheptatriene is known to bind to the $Mo(CO)_3$ fragment more strongly than arenes (by ca. 7 kcal/mol),[13] it should be possible to use an arene exchange reaction to attach the $Mo(CO)_3$ moiety to the seven-membered ring in **12** and **13** (Scheme 4). Indeed, addition of THF-d_8 to a mixture of equivalent amounts of **12**, **13** (6:1), and (η^6-*p*-xylene)-$Mo(CO)_3$ in an NMR tube led to a rapid color change from yellow to deep red. After 15 min, analysis by ^1H and ^{31}P NMR showed total disappearance of starting materials and formation of **5** and **6** (65% isolated yield from benzene/hexane) in a 6:1 ratio which was the same as that of **12** to **13**. In addition to the PPh_3 signals, the ^1H NMR of **5** (the major isomer) exhbited six different proton resonances two of which (at δ 5.4 and 2.4 ppm) showed coupling to the ^{195}Pt nucleus. The peak at δ 5.4 ppm is assigned to the vinyl proton H1 while the peak at δ 2.4 ppm is assigned to the methylene proton Hd. The minor isomer **6** shows four peaks with only one (at δ 4.5 ppm) coupled to the ^{195}Pt nucleus. The peak at δ 4.5 is therefore assigned to H1′. The remaining signals in the spectrum of **5** and **6** are assigned based on a 2D COSY experiment. The proton resonances of both **5** and **6** are shifted upfield relative to **12** and **13**. The $^{195}Pt\{^1H\}$ NMR of the mixture of **5** and **6** shows a doublet of doublets centered at δ −4480.4 ($^1J_{Pt-P'} = 3326.4$ Hz, $^1J_{Pt-P''} = 3418$ Hz) and a triplet at δ −4449 ($^1J_{Pt-P} = 3323$ Hz) as expected for complexes with C_1 (**5**) and C_s (**6**) symmetry, respectively.

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[12] (a) Dunitz, J. D.; Pauling, P. *Helv. Chim. Acta* **1960**, *43*, 2188. (b) Chen, J.; Yin, J.; Lei, G.; Xu, W.; Shao, M.; Zhang, Z.; Tang, Y. *J. Organomet. Chem.* **1987**, *329*, 69. (c) Adams, H.; Bailey, N. A.; Willett, D. G.; Winter, M. J. *J. Organomet. Chem.* **1987**, *333*, 61. (d) Wieser, M.; Sunkel, K.; Robl, C.; Beck, W. *Chem. Ber.* **1992**, *125*, 1369. (e) Breimair, J.; Weidmann, T.; Wagner, B.; Beck, W. *Chem. Ber.* **1991**, *124*, 2431.

[13] Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529.

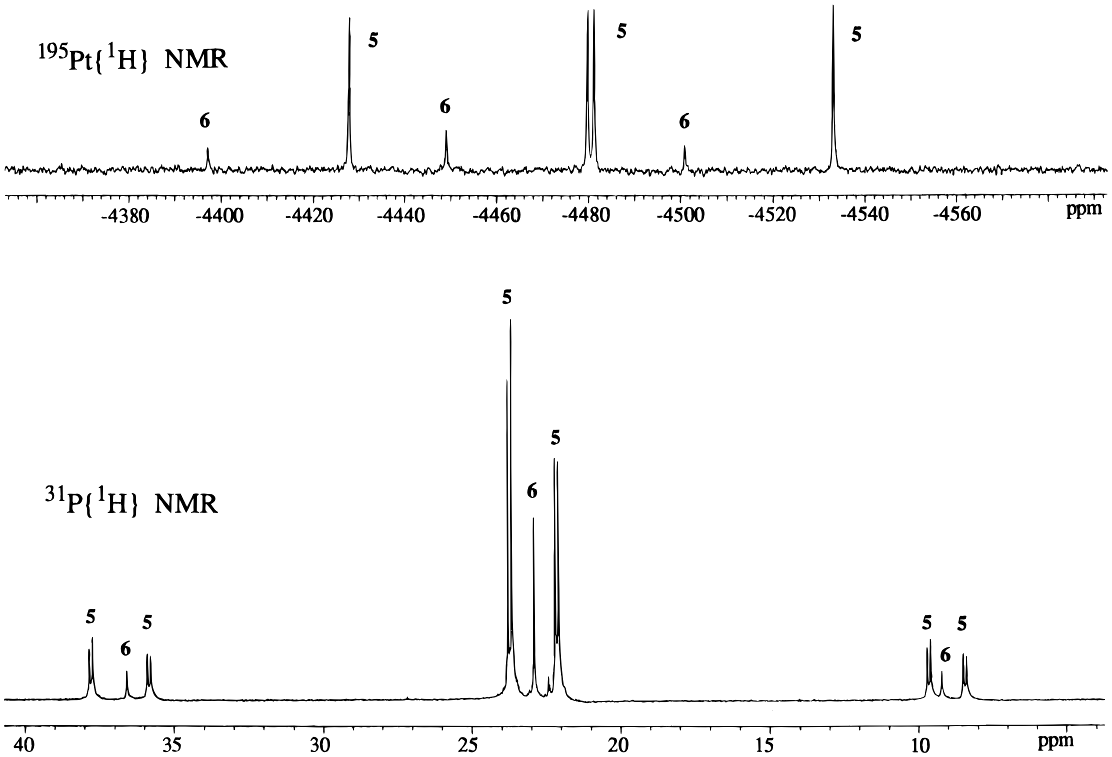


Figure 2. $^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ spectra of a mixture of complexes **5** and **6**.

Table 3. Crystallographic Data

	5	7
A. Crystal Data (298 K)		
a, Å	11.909(2)	9.500(2)
b, Å	29.260(3)	20.346(4)
c, Å	12.033(2)	13.710(4)
β, deg	90.06(1)	110.20(2)
V, Å^3	4193(1)	2487(1)
d_{calc}, g cm^{-3} (298 K)	1.630	1.426
empirical formula	$C_{46}H_{36}O_3P_2MoPt\cdot{}^1/_2C_6H_6$	$C_{46}H_{36}O_3P_2MoPt\cdot C_6H_6$
fw	1028.77	423.11
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$
F(000), electrons	2028	1056
cryst size, mm^3	0.32 × 0.23 × 0.1	0.21 × 0.15 × 0.11
B. Data Collection (298 K)		
radiation (λ, Å)	Mo Kα (0.710 73)	
mode	ω-scan	
scan range	symmetrically over 1.2° about K$\alpha_{1,2}$ max	
background	offset 1.0 and −1.0 in ω from K$\alpha_{1,2}$ max	
scan rate, deg min^{-1}	3−6	3−6
2θ range, deg	3−50	3−55
range of hkl	$0 \le h \le 14$	$-1 \le h \le 12$
	$0 \le k \le 34$	$-4 \le k \le 26$
	$-14 \le l \le 14$	$-17 \le l \le 17$
tot. reflcns measd	7933	8412
unique reflcns	7377	7152
abs coeff μ(Mo Kα), mm^{-1}	3.75	3.16
min, max transm	0.404, 0.722	0.514, 0.723
C. Structure Refinement		
S, goodness-of-fit	1.2	1.45
reflcns used	4330, $I > 3\sigma(I)$	4229, $I > 2.5\sigma(I)$
no. of variables	505	527
R, wR,[a] %	3.81, 4.03	5.49, 5.67
R_{int}, %	1.7	2.34
max shift/esd	0.002	0.031
min peak in diff Fourier map, e Å^{-3}	−1.2	−1
max peak in diff Fourier map, e Å^{-3}	1.1	2.2

[a] Relevant expressions are as follows, where F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes. Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \Sigma(||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

The $^{31}P\{^1H\}$ NMR of **5** and **6** is also consistent with the proposed structures (Figure 2). The room-temperature $^{13}C\{^1H\}$ NMR spectrum of **5** and **6** does not exhibit any signals in the carbonyl region. The spectrum

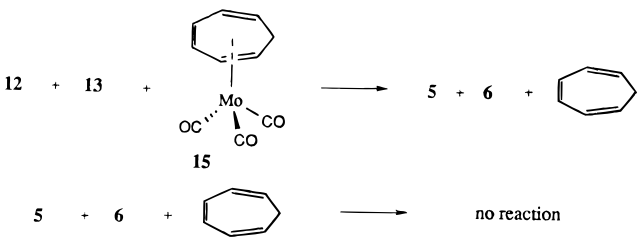
Table 4. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-H Atoms of Complex 7 with Solvent Coordinates Not Included

atom	*x*	*y*	*z*	*U*
Pt	0.94281(7)	0.0	0.98550(4)	0.0384(2)
Mo	0.9845(2)	−0.02742(12)	1.25039(12)	0.0516(7)
P1	0.7398(6)	0.0540(3)	0.8739(4)	0.046(2)
P2	1.0082(6)	−0.0791(3)	0.8899(4)	0.045(2)
O1	0.813(2)	−0.1403(8)	1.1063(12)	0.075(7)
O2	0.705(2)	−0.0293(10)	1.3211(14)	0.112(10)
O3	1.139(2)	−0.1319(8)	1.4207(11)	0.095(9)
C1	1.103(2)	0.008(2)	1.1338(11)	0.048(7)
C2	0.993(2)	0.0487(9)	1.1208(12)	0.043(8)
C3	0.947(3)	0.0814(11)	1.194(2)	0.056(10)
C4	1.030(3)	0.0856(13)	1.302(2)	0.065(11)
C5	1.158(3)	0.0582(15)	1.347(2)	0.088(14)
C6	1.276(3)	0.0361(14)	1.296(2)	0.097(12)
C7	1.221(2)	−0.0154(12)	1.2105(13)	0.066(10)
C8	0.877(2)	−0.0986(12)	1.156(2)	0.047(10)
C9	0.802(2)	−0.0277(12)	1.295(2)	0.069(10)
C10	1.086(3)	−0.0956(14)	1.363(2)	0.076(14)
C21	1.191(2)	−0.1139(10)	0.959(2)	0.057(9)
C22	1.307(3)	−0.1169(12)	0.919(2)	0.066(11)
C23	1.447(4)	−0.144(2)	0.970(2)	0.09(2)
C24	1.466(3)	−0.1720(13)	1.063(2)	0.078(12)
C25	1.356(3)	−0.1727(14)	1.104(2)	0.102(14)
C26	1.220(2)	−0.1435(12)	1.056(2)	0.069(10)
C31	0.894(3)	−0.1488(11)	0.856(2)	0.049(11)
C32	0.955(4)	−0.211(2)	0.858(2)	0.09(2)
C33	0.848(4)	−0.265(2)	0.821(3)	0.14(3)
C34	0.704(3)	−0.2584(14)	0.794(2)	0.090(14)
C35	0.646(3)	−0.2000(14)	0.797(2)	0.10(2)
C36	0.741(3)	−0.1456(13)	0.823(2)	0.066(12)
C41	1.019(2)	−0.0473(10)	0.769(2)	0.048(9)
C42	0.972(3)	−0.0812(14)	0.675(2)	0.074(11)
C43	0.963(3)	−0.059(2)	0.580(2)	0.11(2)
C44	1.018(3)	0.004(3)	0.586(2)	0.11(2)
C45	1.076(3)	0.0449(15)	0.672(2)	0.11(2)
C46	1.073(2)	0.0162(9)	0.769(2)	0.055(10)
C51	0.801(3)	0.1310(11)	0.837(2)	0.045(10)
C52	0.929(3)	0.1606(13)	0.899(2)	0.077(14)
C53	0.990(4)	0.2200(12)	0.868(2)	0.083(14)
C54	0.904(4)	0.2498(15)	0.780(2)	0.077(14)
C55	0.775(3)	0.2253(13)	0.713(2)	0.089(13)
C56	0.720(3)	0.1643(11)	0.745(2)	0.059(10)
C61	0.621(2)	0.0180(10)	0.7501(13)	0.055(9)
C62	0.673(2)	0.012(2)	0.6657(12)	0.067(10)
C63	0.590(3)	−0.0189(14)	0.582(2)	0.087(13)
C64	0.455(3)	−0.0505(14)	0.573(2)	0.086(12)
C65	0.403(2)	−0.0440(12)	0.655(2)	0.082(11)
C66	0.486(2)	−0.009(2)	0.7444(14)	0.078(11)
C71	0.602(2)	0.0756(10)	0.9354(14)	0.053(9)
C72	0.518(3)	0.1319(14)	0.914(2)	0.085(13)
C73	0.417(4)	0.145(2)	0.965(3)	0.09(2)
C74	0.386(3)	0.098(2)	1.023(2)	0.090(14)
C75	0.466(2)	0.0421(13)	1.044(2)	0.072(11)
C76	0.576(2)	0.0303(12)	0.9999(12)	0.063(9)

obtained at −20 °C, however, reveals three carbonyl signals of equal intensity that are assigned to the major isomer **5**. This observation is explained as in the case of **7** as due to rapid rotation of the molybdenum tricarbonyl moiety around the axis perpendicular to the seven-membered ring.

The IR spectrum of the mixture of **5** and **6** shows a medium-size absorption at 1610 cm^{-1} which is assigned to the triple bond coordinated to the metal center in **5**. The same absorption in **12**[9] is at 1710 cm^{-1}, which indicates that coordination of molybdenum to **12** causes a decrease in the bond order of the triple bond. The IR spectrum also shows three very strong bands (1956.7, 1886.8, 1845.7 cm^{-1}) in the metal carbonyl region. Interestingly, these carbonyl stretches have lower frequencies (ca. 15 cm^{-1}) than those of tricarbonylmolybdenum cycloheptatriene (**15**), which suggests that the seven-membered ring in **5** is more electron rich than cycloheptatriene itself.[14]

Scheme 5



To test this suggestion, a mixture of **12** and **13** (6:1; total 1 equiv) was added to 2 equiv of **15** in CD_2Cl_2 in an NMR tube at room temperature and formation of **5** and **6** was monitored by ^1H and ^{31}P NMR (Scheme 5). Within experimental detection, both platinum complexes showed complete conversion to the corresponding $Mo(CO)_3$ complexes, although at different rates. Reaction of **5** was complete within 12 h whereas the minor isomer required 4 days. The reason for this reactivity difference is not clear. In a control experiment (Scheme 5) 1 equiv of **5**, **6** was mixed with 3 equiv of cycloheptatriene and monitored as above. As expected, no reaction was observed even after 1 week at room temperature.

The fact that the $Mo(CO)_3$ moiety transfers from **15** to **12**, **13** and that the equilibrium lies, within detection, exclusively toward the more sterically hindered reagents is clear evidence of the greater basicity of the cycloheptadienyne ring in the bis(triphenylphosphine)platinum complexes when compared with cycloheptatriene. Complexes **5**, **6** reacted rapidly with triphenylcarbenium tetrafluoroborate in CD_2Cl_2 at room temperature to give **4** in high yield (90%, confirmed by $^{31}P\{^1H\}$ and ^1H NMR). In fact hydride abstraction from **5** and **6** is the superior way to prepare **4**. The structure of the major cycloheptadienyne complex (**5**) was confirmed by X-ray.

Crystal Structure of $(PPh_3)_2Pt[\eta^2(\eta^6\text{-}C_7H_6)Mo(CO)_3]$ (5). A deep red crystal suitable for X-ray diffraction study was obtained from a mixture of hexane and benzene at 4 °C. A thermal ellipsoid drawing of **5** is depicted in Figure 3, while crystal data are listed in Table 3. Selected bond distances and angles and final fractional atomic coordinates are provided in Tables 2 and 5, respectively. Complex **5** crystallized in monoclinic, centrosymmetric space group $P2_1/n$. The geometry around the Pt atom is square planar with the Pt atom coordinated to two P atoms and two carbon atoms belonging to the seven-membered ring. The C1−C2 distance is 1.292(14) Å and is comparable to other platinum cycloalkyne complexes.[15] Six carbons (C1−C6) of the seven-membered ring are almost coplanar (maximum deviation from the least-squares plane is 0.02(1) Å for C4) whereas the C7 is 0.44(1) Å above this plane. The dihedral angle between planes defined by C1−C2−C3−C4−C5−C6 and C1−C7−C6 is 150(1)°. This angle is significantly larger than the corresponding angle (128 and 138°)[12] in any other reported molybdenum cycloheptatriene complexes. It is thought that the reason for this difference lies in the hybridization at C1

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[14] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1988; p 60.

[15] Robertson, G. B.; Whimp, P. O. *J. Am. Chem. Soc.* **1975**, *97*, 1051.

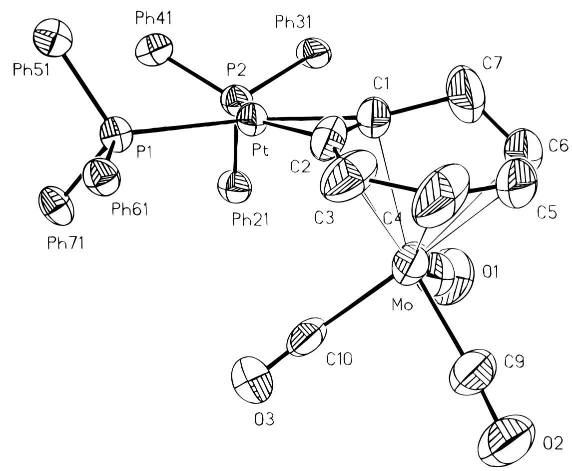

Figure 3. Structure and labeling scheme for **5** with 40% probability of thermal ellipsoids. Triphenylphosphine phenyl rings are omitted for clarity.

and C2, which is intermediate between sp and sp^2. Because of the sp character of C1 and C2 the bond angles about these atoms tend to be larger than 120° which results in flattening of the seven-membered ring.

Attempts To Release 11 from 7. As mentioned above, methods that were successful for the preparation of **12** and **13** failed to yield **11**. As a possible source of **11**, $Mo(CO)_3$ removal from **7** was therefore explored. From the outset it was recognized that this goal provided a special challenge since any reagent used to effect $Mo(CO)_3$ displacement must either be inert to platinum or give a nonproductive reaction. 1,10-Phenanthroline appeared to qualify in the first category because it does not displace PPh_3 from platinum but is known to react with **15** displacing cycloheptatriene.[16] Indeed, as a test case, addition of 1,10-phenanthroline to a mixture of **5** and **6** gave a good recovery of **12** and **13**. As expected, this reaction is much slower for **5** and **6** at room temperature ($t_{1/2}$ for **5** = ca. 2 days, $t_{1/2}$ for **6** = ca. 6 days) than the corresponding reaction with **15**, which, under the same conditions, is complete within minutes. Unfortunately, **7** showed no detectable reaction with phenanthroline, even after several days at room temperature. Similarly, treatment of a mixture of **5** and **6** with 3.5 equiv of PPh_3 led to displacement of $Mo(CO)_3$ (presumably concomitant with nonproductive PPh_3 exchange) but, again, much slower than displacement from **15**; $t_{1/2}$ for **5** at room temperature = ca. 3 days and $t_{1/2}$ for **6** at room temperature = ca. 2 weeks while reaction with **15** was complete within minutes. However, as with the phenanthroline, **7** showed no detectable reaction with PPh_3, even after 1 week at room temperature. These reactivity differences qualitatively correlate with the CO absorptions in the infrared, which, in turn, presumably reflect differences in triene basicities. Steric resistance from the $(Ph_3P)_2Pt$ moiety might also retard $Mo(CO)_3$ displacement from **5**−**7** relative to **15**.

Table 5. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-H Atoms of Complex 5 with Solvent Coordinates Not Included

atom	*x*	*y*	*z*	*U*
Pt	0.02666(3)	0.103410(10)	0.40757(3)	0.04087(10)
Mo	−0.12729(9)	0.08044(3)	0.15654(7)	0.0709(4)
P1	−0.0100(2)	0.17023(7)	0.4972(2)	0.0395(7)
P2	0.2192(2)	0.09954(8)	0.4152(2)	0.0447(7)
O1	0.1030(9)	0.0571(3)	0.0463(8)	0.122(5)
O2	−0.2232(9)	0.0938(3)	−0.0809(7)	0.127(5)
O3	−0.0907(7)	0.1858(3)	0.1378(6)	0.084(3)
C1	−0.0474(9)	0.0497(3)	0.3291(8)	0.063(4)
C2	−0.1233(8)	0.0797(3)	0.3530(7)	0.055(4)
C3	−0.2372(9)	0.0862(4)	0.3210(8)	0.082(5)
C4	−0.2912(11)	0.0560(6)	0.2490(10)	0.112(7)
C5	−0.244(2)	0.0178(5)	0.1962(13)	0.127(9)
C6	−0.141(2)	−0.0018(5)	0.1986(12)	0.123(9)
C7	−0.0510(12)	0.0008(4)	0.2861(11)	0.114(7)
C8	0.0162(12)	0.0669(4)	0.0858(10)	0.088(6)
C9	−0.1907(11)	0.0876(4)	0.0085(10)	0.091(5)
C10	−0.1023(9)	0.1482(4)	0.1474(7)	0.060(4)
C21	0.2862(7)	0.1293(3)	0.2993(7)	0.048(3)
C22	0.3963(8)	0.1441(3)	0.2999(8)	0.061(4)
C23	0.4433(9)	0.1640(4)	0.2084(10)	0.078(5)
C24	0.3820(10)	0.1700(4)	0.1131(9)	0.079(5)
C25	0.2739(10)	0.1572(4)	0.1113(9)	0.086(5)
C26	0.2253(8)	0.1368(3)	0.2036(8)	0.059(4)
C31	0.2770(8)	0.0421(3)	0.4029(7)	0.052(3)
C32	0.3877(9)	0.0338(4)	0.3812(10)	0.082(5)
C33	0.4269(11)	−0.0104(4)	0.3685(11)	0.099(6)
C34	0.3606(12)	−0.0464(4)	0.3798(10)	0.100(6)
C35	0.2513(13)	−0.0388(4)	0.4071(12)	0.112(6)
C36	0.2092(9)	0.0049(3)	0.4179(9)	0.074(4)
C41	0.2925(7)	0.1221(3)	0.5389(7)	0.048(3)
C42	0.3205(8)	0.0930(3)	0.6246(8)	0.063(4)
C43	0.3662(9)	0.1102(5)	0.7215(9)	0.086(5)
C44	0.3835(9)	0.1558(5)	0.7343(10)	0.086(5)
C45	0.3564(8)	0.1849(4)	0.6486(9)	0.070(4)
C46	0.3105(7)	0.1685(3)	0.5505(8)	0.058(4)
C51	−0.0010(7)	0.1685(3)	0.6479(7)	0.043(3)
C52	0.0563(7)	0.1335(3)	0.6990(7)	0.053(3)
C53	0.0685(9)	0.1312(4)	0.8112(8)	0.067(4)
C54	0.0194(9)	0.1632(4)	0.8755(9)	0.078(5)
C55	−0.0409(8)	0.1986(4)	0.8313(8)	0.061(4)
C56	−0.0510(7)	0.2012(3)	0.7159(8)	0.054(3)
C61	−0.1565(6)	0.1883(3)	0.4789(7)	0.040(3)
C62	−0.1887(7)	0.2221(3)	0.4039(8)	0.060(4)
C63	−0.3010(9)	0.2329(4)	0.3902(9)	0.080(5)
C64	−0.3819(8)	0.2107(4)	0.4528(9)	0.073(4)
C65	−0.3516(8)	0.1769(3)	0.5246(9)	0.065(4)
C66	−0.2394(7)	0.1662(3)	0.5384(8)	0.057(4)
C71	0.0671(7)	0.2212(3)	0.4540(8)	0.045(3)
C72	0.0891(7)	0.2253(3)	0.3405(8)	0.057(4)
C73	0.1422(8)	0.2635(4)	0.2976(9)	0.077(5)
C74	0.1752(9)	0.2973(4)	0.3692(11)	0.080(5)
C75	0.1592(8)	0.2926(3)	0.4809(11)	0.077(5)
C76	0.1050(7)	0.2553(3)	0.5228(8)	0.059(4)

Experimental Section

General Considerations. All experiments involving organometallic compounds were carried out under an atmosphere of purified N_2 using Schlenk, vacuum line, and drybox techniques. Solvents were distilled under nitrogen prior to use, toluene, THF, and Et_2O from sodium benzophenone ketyl, hexane from sodium benzophenone ketyl/tetraglyme mixture, and methylene chloride from CaH_2. NMR spectra were measured on a Varian XL-300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C; 282 MHz, ^{19}F; 121 MHz, ^{31}P; 64 MHz, ^{195}Pt). ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are referenced to the residual solvent peaks and are reported in ppm relative to tetramethylsilane. ^{19}F NMR spectra are referenced to external $CFCl_3$. $^{31}P\{^1H\}$ NMR spectra are referenced to external 85% H_3PO_4 in D_2O. $^{195}Pt\{^1H\}$ NMR spectra are referenced to an external saturated solution of Na_2PtCl_4 in D_2O. All *J* values are given in Hz. Infrared spectra were measured on a Perkin-Elmer 1600 FTIR spectrometer. Mass spectra (positive FAB) were obtained on the Finnigan Mat 95Q. Elemental analyses were performed in the microanalysis laboratory in the Chemistry Department at the University of Florida. Melting points were measured in open capillaries and are not corrected. Triphenylcarbenium

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(16) Behrens, H.; Lindner, E.; Lehnert, G. *J. Organomet. Chem.* **1970**, *22*, 439.

tetrafluoroborate, 1,10-phenanthroline, and 1 M THF solutions of $KBEt_3H$ and $LiAl(O^tBu)_3H$ were purchased from Aldrich Chemical Co. All compounds were used as received. The following compounds were prepared as described in the literature, without any modification: (η^6-*p*-xylene)$Mo(CO)_3$,[17] $(PPh_3)_2Pt(\eta^2$-$C_7H_6)$ (**12**, **13**).[9]

Preparation of $(PPh_3)_2Pt[\eta^2(\eta^6$-$C_7H_6)Mo(CO)_3]$ (5, 6). A Schlenk tube was charged with 0.56 g (0.692 mmol) of **12** and **13** and 0.198 g (0.692 mmol) of (η^6-*p*-xylene)$Mo(CO)_3$. To this mixture was added 25 mL of THF at room temperature. The Schlenk tube was wrapped with aluminum foil, and the mixture was stirred for 20 min at room temperature. The solvent was evaporated in vacuum, and the residue was dissolved in 20 mL of benzene. To this solution was added 35 mL of hexane, and the solution was filtered through a cannula into another Schlenk tube. The Schlenk tube was placed in the freezer (−16 °C) for 1 day. The supernatant was decanted leaving 0.44 g of red crystals (61.7% yield, 6:1 for **5**:**6**), mp 147−149 °C (dec). IR (KBr): 3052 w, 2802 w, 1956.7 s (CO), 1886.8 s (CO), 1845.7 s (CO), 1610.7 m (coordinated CC), 1479.7 m, 1302 w, 1183.5 w, 1159.6 w, 1095.5 m, 1027.9 w, 744 m, 695 s, 523 s cm^{-1}. HRMS (FAB): calcd for $(M + 1)^+$, *m*/*e* 992.0921; found, 992.0959. Anal. Calcd for $C_{46}H_{36}O_3P_2MoPt$; $0.5C_6H_6$: C, 57.21; H, 3.82. Found: C, 57.22; H, 3.76. Data for complex **5** are as follows. ^1H NMR (CD_2Cl_2): δ 7.1−7.5 (m, 30H, PPh_3), 6.10 (td, 1H, $^3J_{H2-H3} = 7.1$ Hz, $^3J_{H2-H1} = 3.1$ Hz, H2), 5.55 (dd, 1H, $^4J_{H1-P} = 6.2$ Hz, $^3J_{H1-H2} = 3.7$ Hz, $^3J_{H1-Pt} = 40.2$, H1), 4.47 (t, $^3J_{H3-H2,4} = 8$ Hz, H3), 4.13 (p, 1H, $J_{H-H} = 4$ Hz, H4), 3.51 (dtd, 1H, $^2J_{Hd-Hu} = 15.7$ Hz, $^3J_{Hd-H} = 5.4$ Hz, $J_{Hd-H} = 1.8$ Hz, $^3J_{Hd-Pt} = 59.4$ Hz, Hd), 3.21 (dd, 1H, $^2J_{Hu-Hd} = 15.7$ Hz, $J_{Hu-H} = 1.4$ Hz, Hu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C): δ 229.69, 221.37, 218.74, 135.6 (qd, $J = 22.5$ Hz, $J = 1.8$ Hz, PPh_3-ipso), 134.25 (m, PPh_3), 129.95 (s, PPh_3-para), 128.26 (m, PPh_3), 103.03, 100.47 (dd, $^2J_{C-Pcis} = 7$ Hz, $^2J_{C-Ptrans} = 83.5$ Hz), 98.19 (d, $J_{C-P} = 10.3$ Hz, $J_{C-Pt} = 54.7$), 97.2 (dd, $^2J_{C-Pcis} = 4.7$ Hz, $^2J_{C-Ptrans} = 83.6$ Hz), 82.41 (t, $J_{C-P} = 8.5$), 75.63 (d, $J_{C-P} = 7.5$, $J_{C-Pt} = 48.3$), 29.12 (t, $J_{C-P} = 8$). ^{31}P NMR (CD_2Cl_2): δ 22.15 (d, $^2J_{P'-P''} = 13.8$ Hz), 23.73 (d, $^2J_{P'-P''} = 13.8$ Hz). ^{195}Pt NMR (CD_2Cl_2): δ −4480.4 (dd, $^1J_{Pt-P'} = 3326.4$ Hz, $^1J_{Pt-P''} = 3418$ Hz). Data for complex **6** are as follows. ^1H NMR (CD_2Cl_2): δ 7.1−7.5 (m, 30H, PPh_3), 4.99 (br d, 2H, $^3J_{H1'-H2'} = 7.2$ Hz, $^3J_{H1'-Pt} = 30$ Hz, H1′), 3.37 (m, 2H, H2′), 2.92 (dt, 1H, $^2J_{Hd-Hu} = 13.2$ Hz, $J_{Hd-H1'} = 8.6$ Hz, Hd), 2.36 (br d, 1H, $^2J_{Hu-Hd} = 13.2$ Hz, Hu). ^{13}C NMR (CD_2Cl_2): δ 97.53, 56.19 (t, $J_{C-P} = 8.1$), 28.93. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.91 (s). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ −4449 (t, $^1J_{Pt-P} = 3323$ Hz).

Preparation of $(PPh_3)_2Pt[\eta^2(\eta^7$-$C_7H_5)Mo(CO)_3]$ (4). Method I. A 27 mg (0.03 mmol) amount of **1** was dissolved in 0.3 mL of THF-d_8 and 0.3 mL of CD_2Cl_2. To this solution was added 12 mg (0.042 mmol) of (η^6-*p*-xylene)$Mo(CO)_3$. The color started to change at once from red to brown red; 20 min after the addition the ^1H and $^{31}P\{^1H\}$ NMR showed virtually quantitative formation of **4**.

Method II. A 230 mg (0.223 mmol) amount of **5** and **6** was dissolved in 10 mL of CH_2Cl_2 in a Schlenk tube wrapped in aluminum foil. To this solution 82 mg (0.248 mmol) of triphenylcarbenium tetrafluoroborate dissolved in 3 mL of CD_2Cl_2 was added dropwise at room temperature. After 1 h of stirring 20 mL of hexane was added and the solution was filtered. To the filtrate more hexane (30 mL) was added, and the Schlenk tube was placed in the freezer (−16 °C). After 1 day the supernatant was decanted leaving a red oil which solidified after applying a vacuum (200 mg, 80% yield). This solid was at least 95% pure as shown by NMR (see Supporting Information for ^1H, ^{31}P, and ^{195}Pt spectra), mp 97−99 °C (dec). Unfortunately, **4** could not be obtained either as an analytically pure material nor could a single crystal suitable for X-ray diffraction be grown. IR (KBr): 3025 w, 2036.2 s (CO), 1976.2 br, s (CO), 1550 w, 1481.3 m, 1436.4 s, 1097 s, 1083 br s, 1058 br s, 746 m, 695 s cm^{-1}. HRMS (FAB): calcd for M^+, *m*/*e* 990.0765; found, *m*/*e* 990.0645. ^1H NMR (CD_2Cl_2): δ 7.25−7.45 (m, 30H, PPh_3), 6.10 (m, 1H, H2), 5.65 (t, 1H, $^3J_{H1-H2} = 10.8$ Hz, H3), 5.55 (t, 1H, $^3J = 5.8$ Hz, $^3J_{H1-Pt} = 36.7$ Hz, H1). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ 212.02 (s, CO), 133.56 (d, $J_{C-P} = 12.6$ Hz, PPh_3), 132.10 (d, $^1J_{C-P} = 51.3$ Hz, PPh_3-ipso), 130.86 (s, PPh_3-para), 128.48 (d, $J_{C-P} = 10.5$ Hz, PPh_3), 111.28 (dd, $^2J_{C-Pcis} = 4.3$ Hz, $^2J_{C-Ptrans} = 93.6$ Hz, C4), 100.75 (d, $J_{C-P} = 10.7$ Hz, $J_{C-Pt} = 50.4$, C2), 97.96 (s, C3), 87.08 (t, $J_{C-P} = 7.9$, C1). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.25 (s). ^{19}F NMR (CD_2Cl_2): δ −152.78 (s). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ −4087.6 (t, $^1J_{Pt-P} = 3267$ Hz).

Preparation of $(PPh_3)_2Pt[\eta^2(\eta^6$-$C_7H_6)Mo(CO)_3]$ (7). A 250 mg (0.224 mmol) amount of **4** was dissolved in 7 mL of THF, and the Schlenk tube was cooled to −78 °C. To this solution was added slowly 250 mL of a 1 M solution of $LiAl(O^tBu)_3H$ dissolved in 2 mL of THF. During addition the color changed noticeably from red-brown to deep red. The mixture was stirred at low temperature for 20 min and then was warmed to room temperature. The solvent was removed in vacuum and the residue dissolved in 10 mL of benzene followed by addition of 15 mL of hexane. The solution was filtered and placed in the freezer (−16 °C). After a few days red crystals were collected (120 mg, 42% yield), mp 133−136 °C (dec). IR (KBr): 3052 w, 2828 w, 1947 s (CO), 1870.8 s (CO), 1847 s (CO), 1560 m, 1478.5 m, 1434 w, 1385 m, 1095.8 m, 745.6 m, 694.4 s, 678 s cm^{-1}. HRMS (FAB): calcd for $(M + 1)^+$, *m*/*e* 992.0921; found, *m*/*e* 992.1014. Anal. Calcd for $C_{46}H_{36}O_3P_2MoPt \cdot C_6H_6$: C, 58.49; H, 3.96. Found: C, 58.53; H, 4.05. ^1H NMR (CD_2Cl_2): δ 7.1−7.45 (m, 30H, PPh_3), 5.84 (td, 1H, $J = 1.2$ Hz, $J = 5$ Hz, $^3J_{H1-Pt} = 44.4$, H1), 4.90 (m, H2), 3.85 (td, 1H, $J = 1.5$ Hz, $J = 6.3$ Hz, $^3J_{H4-Pt} = 50.4$, H4), 3.17 (m, H3), 3.08 (m, Hd), 2.49 (d, 1H, $^2J_{Ha-Hd} = 12.3$ Hz, Hu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 224.8 [−50 °C, 231.83, 222.52, 218.31], 135.12 (d, $^1J_{C-P} = 4.6$ Hz, PPh_3-ipso), 134.42 (m, PPh_3), 130.31 (dd, $J_{C-P} = 2.3$ Hz, $J_{C-P} = 5.3$ Hz, PPh_3-para), 128.47 (m, PPh_3), 112.15 (dd, $^2J_{C-Pcis} = 7.5$ Hz, $^2J_{C-Ptrans} = 90.5$ Hz), 107.13 (d, $J_{C-P} = 10.6$ Hz, $J_{C-Pt} = 68.3$), 102.10 (dd, $^2J_{C-Pcis} = 7.5$ Hz, $^2J_{C-Ptrans} = 83$ Hz), 86.93 (t, $J_{C-P} = 8.3$ Hz), 62.81, 48.5 (t, $J_{C-P} = 9.1$ Hz), 29.99 (d, $J_{C-P} = 8.3$, $J_{C-Pt} = 44.5$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.81 (d, $^2J_{P'-P''} = 9.2$ Hz), 23.55 (d, $^2J_{P'-P''} = 9.2$ Hz). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ −4420.2 (dd, $^1J_{Pt-P'} = 3124$ Hz, $^1J_{Pt-P''} = 3282.5$ Hz).

Reaction of 7 with Triphenylcarbonium Tetrafluoroborate. A 20 mg (0.02 mmol) amount of **7** and 7 mg (0.021 mmol) of triphenylcarbenium tetrafluoroborate were dissolved in 0.5 mL of CD_2Cl_2. After 15 min NMR measurements (^1H and $^{31}P\{^1H\}$) showed clean formation of **4** (spectroscopic data were identical to those of the compound obtained from hydride abstraction from **5** and **6**).

Reaction of 12, 13 with (η^6-C_7H_8)$Mo(CO)_3$ (15). A 50 mg (0.062 mmol) of amount **12**, **13** and 17 mg (0.062 mmol) of **15** were placed in an NMR tube equipped with a PTFE valve and dissolved in 0.5 mL of CD_2Cl_2. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR. The major isomer (**12**) reacted within 12 h whereas the minor one (**13**) required 4 days. On the basis of ^{31}P NMR, the final reaction mixture consisted of predominantely **5**, **6** with a small amount of other unidentified phosphorus-containing products.

Reaction of 5, 6 with 1,10-Phenanthroline. A 50 mg (0.05 mmol) amount of **5**, **6** and 19 mg (0.11 mmol) of 1,10-phenanthroline were dissolved in 0.5 mL of CD_2Cl_2. The major isomer (**5**) reacts faster ($t_{1/2} = 2$ days) than the minor one (**6**) ($t_{1/2} = 6$ days) to give a mixture of **12** and **13**. On the basis of ^{31}P NMR, the final reaction mixture consisted of almost exclusively **12**, **13** contaminated with a small amount of other unidentified phosphorus-containing products.

Reaction of 5, 6 with Triphenylphosphine. A 50 mg (0.05 mmol) amount of **5**, **6** and 45 mg (0.18 mmol) of triphenylphosphine were dissolved in 0.5 mL of CD_2Cl_2. The major isomer (**5**) reacts faster ($t_{1/2} = 3$ days) than the minor one (**6**) ($t_{1/2} = 2$ weeks) to give a mixture of **12** and **13**. On the basis of ^{31}P NMR, the final reaction mixture consisted of

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[17] Strohmeier, W. *Chem. Ber.* **1961**, *94*, 3337.

primarily **12**, **13** contaminated with a small amount of other unidentified phosphorus-containing products.

Crystallographic Analysis for 5 and 7. Data for both complexes were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å). In each case, 32 reflections with $20.0° \le 2\theta \le 22.0°$ were used to refine the respective cell parameters. Totals of 7933 and 8412 reflections, for **5** and **7**, respectively, were collected using the ω-scan method. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was **1** and **4**%, for **5** and **7**, respectively). Absorption corrections were applied on the basis of the measured crystal faces using SHELXTL plus,[18] the absorption coefficient, μ, was 3.75 and 3.16 mm^{-1}, for **5** and **7**, respectively (minimum and maximum transmission factors are 0.404 and 0.722 for **5** and 0.514 and 0.723 for **7**, respectively).

Both structures were solved by the heavy-atom method in SHELXTL plus[17] from which the locations of the heavy atoms were obtained. The rest of the non-hydrogen atoms were obtained from subsequent difference Fourier maps. The structures were refined in SHELXTL plus using full-matrix least squares. The non-H atoms of the complexes were treated anisotropically, whereas the benzene molecules C atoms of **7** were refined with isotropic thermal parameters; the C atoms of the benzene molecule in **5** were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated in ideal positions, and their isotropic thermal parameters were fixed. The asymmetric unit of **5** contains the complex and one half of a benzene molecule of crystallization, while the asymmetric unit of **7** contains one complex and two partial benzene molecules of crystallization. The site-occupation factors of these benzene molecules were dependently refined. One refined to 0.55(1), and consequently the other partial benzene has an occupation factor of 0.45(1). In the final cycle of refinement of **5**, 4330 reflections with $F > 6\sigma(F)$ gave R and wR values of 3.81 and 4.03%, respectively. For **7**, 4229 reflections with $F > 5\sigma(F)$ gave R and wR values of 5.49 and 5.67%, respectively. Since the space group $P2_1$ is chiral, the absolute configuration of the structure was determined by refining the other enantiomer with the same data. This refinement yielded R and wR values of 6.27 and 7.10%, respectively. Using the Hamilton[19] test, the structure of the enantiomer was rejected at a confidence level of 99.95%. Additionally, the chirality/polarity[20] factor η (a factor multiplying f'') was refined to 0.40(3). The η value should normally refine to 1 with a small esd for the correct enantiomer or -1 for the wrong enantiomer. Perhaps η did not refine to a value of 1 for **7** because of the small number of Friedel relative reflections that were collected. The linear absorption coefficient was calculated from values from ref 21. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann[22] with anomalous-dispersion corrections from Cromer and Liberman,[23] while those of hydrogen atoms were from Stewart, Davidson, and Simpson.[24]

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Supporting Information Available: ^{1}H, ^{31}P, and ^{195}Pt NMR spectra of **4** and thermal ellipsoid drawings showing full numbering schemes and tables of atomic positional and thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and comprehensive bond lengths and angles (25 pages). Ordering information is given on any current masthead page.

OM950732D

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