

Selective Lithiation and Phosphane-Functionalization of $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]$ (Troticene) and Its Use for the Preparation of Early-Late Heterobimetallic Complexes

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Abstract: The cycloheptatrienyl-cyclopentadienyl sandwich complex $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]$ (troticene) can be dilithiated (once at each ring) or selectively monolithiated, either at the seven- or five-membered ring, depending on the reaction conditions. Treatment of the resulting lithiotroticenes with ClPPh_2 afforded the corresponding troticenylium-phosphanes $[(\eta^7\text{-C}_7\text{H}_6\text{PPh}_2)\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)]$ (**1**), $[(\eta^7\text{-C}_7\text{H}_6\text{PPh}_2)\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**), or $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)]$ (**3**). The use of $n\text{BuLi}/N,N,N',N'$ -pentamethyldiethylenetriamine (pmdta) allowed us to isolate the lithium complexes $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})]\cdot\text{pmdta}$ (**4**) and $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})]\cdot\text{pmdta}$ (**5**), which were structurally characterized by X-ray diffraction analyses. Reaction of the monophosphane **3** with $\text{Mo}(\text{CO})_6$ and $[(\text{tht})\text{AuCl}]$ (tht = tetrahydrothiophene) afforded the heterobimetallic complexes $[(\text{3})\text{Mo}(\text{CO})_5]$ (**6**) and $[(\text{3})\text{AuCl}]$ (**7**) and also the trimetallic species $[(\text{3})_2\text{AuCl}]$ (**8**). The reaction of $\text{trans-}[\text{PtCl}_2(\text{SEt}_2)_2]$ with the diphosphane **1** led to the formation of $\text{cis-}[(\text{1})\text{PtCl}_2]$ (**9**), whereas the complexes $\text{trans-}[(\text{2})_2\text{PtCl}_2]$ (**10**) and $\text{trans-}[(\text{3})_2\text{PtCl}_2]$ (**11**) were isolated by reaction of two equivalents of the monophosphanes **2** and **3** with $\text{trans-}[\text{PtCl}_2(\text{SEt}_2)_2]$. The X-ray crystal structures of **6–11** are also reported.

Introduction

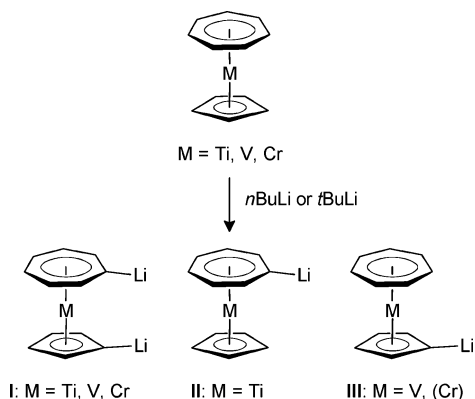
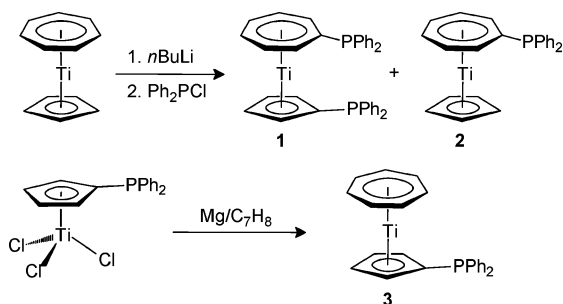
Ever since the first isolation of ferrocene,¹ this compound has displayed a wide range of intriguing and useful forms of chemical reactivity,² and its modification has become an important task in organometallic chemistry.³ Lithiation at the cyclopentadienyl rings proved to be of particular importance for the functionalization of the ferrocene moiety,^{4,5} and consequently, lithioferrocenes are often encountered as intermediates in the synthesis of ferrocenyl mono- and diphosphane ligands,⁶ which have attracted considerable attention because of their relevance for a number of transition metal-catalyzed reactions.^{2,6}

In stark contrast, the modification of other sandwich complexes is significantly less developed and, for instance, little use has been made of sandwich complexes containing cycloheptatrienyl (Cht) ligands, even though mixed cycloheptatrienyl–cyclopentadienyl (Cht–Cp) complexes of the type $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\eta^5\text{-C}_5\text{H}_5)]$ (M = group 4–6 metals) have been known for more than three decades.⁷ Only recently,⁸ the interest in these early transition metal Cht–Cp complexes has become revitalized by independent reports from Elschenbroich, Braunschweig and Tamm on the preparation of *ansa*-Cht–Cp complexes,^{9–11} which involved in all cases the generation of dilithio complexes $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{M}(\eta^5\text{-C}_5\text{H}_4\text{Li})]$ (M = Ti, V, Cr) of type **I** (Scheme 1) in the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda).

Clearly, dilithiation can be achieved conveniently for all three Cht–Cp complexes, troticene (M = Ti), trovacene (M = V) and trochrocene (M = Cr), and it should be noted that

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Scheme 1. Lithiation of Cycloheptatrienyl–Cyclopentadienyl Sandwich complexes**Scheme 2.** Preparation of Phosphane-Functionalized Tropicenes

dilithiation of tropicene had been observed for the first time as early as 1974 by de Liefde Meijer.¹² Fifteen years later, Rausch and co-workers provided a viable protocol for the isolation of the titanium species $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})]\cdot\text{tmeda}$ and its use for the preparation of tropicenyl diphosphane ligands such as $[(\eta^7\text{-C}_7\text{H}_6\text{PPh}_2)\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)]$ (dppti, **1**) (Scheme 2).^{13,14} Surprisingly, the picture is much less clear-cut for the monolithio complexes $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{M}(\eta^5\text{-C}_5\text{H}_5)]$ (**II**) and $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\eta^5\text{-C}_5\text{H}_4\text{Li})]$ (**III**): For tropicene, monolithiation was reported to proceed exclusively at the seven-membered ring (Scheme 1, type **II**),^{12,14} which allowed, inter alia, the selective synthesis of tropicenyl monophosphanes such as $[(\eta^7\text{-C}_7\text{H}_6\text{PPh}_2)\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**).¹⁵ In contrast, lithiation of trovacene was achieved exclusively at the five-membered ring, and the resulting $[(\eta^7\text{-C}_7\text{H}_7)\text{V}(\eta^5\text{-C}_5\text{H}_4\text{Li})]$ intermediate (Scheme 1, type **III**) was mainly involved in the preparation of numerous poly(trovacenes) that were used to study the intermetallic communication (exchange coupling) between the resulting paramagnetic 17-

electron sandwich moieties.¹⁶ Finally, reports on the monometalation of trochrocene are scarce, and we are only aware of an early report from Fischer and Breitschaft, who observed that metalation with amyl sodium occurred mainly, but not exclusively, at the five-membered ring.¹⁷ However, the yields were reported to be extremely low, and no metalation at all was achieved by the use of lithium reagents such as PhLi or $n\text{BuLi}$.^{12,17}

Since monolithiation of tropicene was reported to occur exclusively at the seven-membered ring (*vide supra*), only the tropicenyl phosphane **2** was previously accessible by this route.¹⁵ Only recently, we reported a method for the synthesis of the isomeric phosphane $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)]$ (**3**), which involved the reduction of the half-sandwich complex $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)\text{TiCl}_3]$ with magnesium in the presence of cycloheptatriene (Scheme 2).¹⁸ It should be noted, however, that preparation of this starting material and of the phosphane-functionalized cyclopentadienyl ligand precursor is rather tedious and requires two lithiation steps. Accordingly, direct functionalization of tropicene at the five-membered ring would be advantageous and would also allow direct access to other functionalized tropicene species, and we therefore became interested in reinvestigating the lithiation of tropicene with the objective of gaining full control over the selectivity of this reaction. As a result, we report herein the selective mono- and dilithiation of tropicene and its use for the high-yield preparation of the phosphane ligands **1**, **2**, and **3** together with a number of their transition metal complexes. In addition, the X-ray crystal structures of lithio complexes of type **I** and **III** are provided.

Results and Discussion

Dilithiation of Tropicene. Although the dilithiation of tropicene with n -butyllithium and tmeda is well-established, we were interested in identifying the optimum conditions for the generation of dilithiotropicene $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})]$ and also in structurally characterizing this reactive intermediate. In our hands, the best results were obtained when the preformed lithiating reagent, prepared from equimolar amounts of n -butyllithium and N,N',N'',N''' -pentamethyldiethylenetriamine (pmdta), is slowly added to a suspension of tropicene in hexane, followed by stirring overnight. Filtration and washing with hexane afforded a green pyrophoric solid in high yield (86%), which can be stored for several days under an inert atmosphere at room temperature. As indicated by elemental analysis, this material has the composition $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})]\cdot\text{pmdta}$ (**4**) and is sufficiently pure to be used directly for further transformations.

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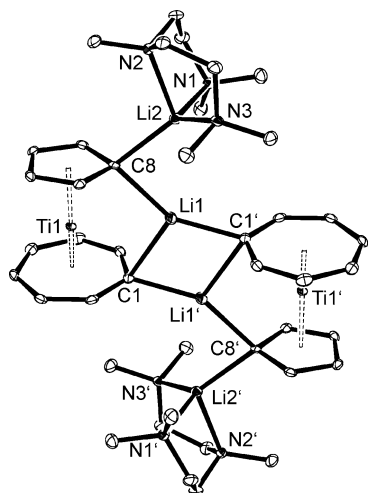
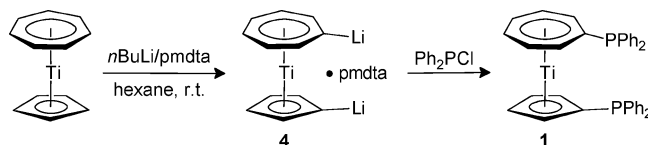


Figure 1. ORTEP view of $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})]_2 \cdot 2\text{pmdta}$ (**4**). Molecule **1** is shown, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for molecule **1**: Li1–C1 2.246(3), Li1–C1' 2.126(3), Li1–C8 2.170(3), Li2–C8 2.150(3), Li2–N1 2.115(3), Li2–N2 2.095(3), Li2–N3 2.120(3), Ti–C_{cht} 2.175(2)–2.219(2), Ti–C_{cp} 2.292(2)–2.356(2); C1–Li1–C1' 110.59(13), C1–Li1–C8 101.69(12), C8–Li1–C1' 147.29(14), Li1–C1–Li1' 69.41(13), Li1–C8–Li2 83.05(11), N1–Li2–N2 88.02(11), N1–Li2–N3 116.58(13), N2–Li1–N3 87.02(11).

The composition of **4** was also confirmed spectroscopically; the ^1H NMR spectrum exhibits three broad multiplets for the Cht ($\delta = 6.24, 5.99, \text{ and } 5.62$ ppm) and a broad multiplet for the Cp hydrogen atoms ($\delta = 5.89$ ppm), which is for both rings downfield from the corresponding trocicene resonances ($\delta = 4.90, \text{ C}_5\text{H}_5; \delta = 5.42$ ppm, C_7H_7). Furthermore, the isolation of suitable single crystals of **4**·toluene from a saturated toluene solution at -30 °C allowed us to determine the X-ray crystal structure of **4**. The asymmetric unit contains two halves of two independent centrosymmetric complexes of the type $[(\eta^7\text{-C}_7\text{H}_6\text{Li})\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li})]_2 \cdot 2\text{pmdta}$ (and one toluene molecule), and Figure 1 shows the complete molecule **1** as a representative of the two structurally closely related dimers. In each molecule, the trocicene units are connected by two symmetry-equivalent bridging lithium atoms (Li1/Li1' in molecule **1**, Li3/Li3' in molecule **2**). Each independent lithium atom is bound to one carbon atom of each equivalent C_7H_6 ring (Li1 to C1/C1', Li3 to C22/C22') and to one carbon atom (Li1 to C8, Li3 to C29) of the independent C_5H_4 ring, affording a central Li_2C_2 rhomboid with lithium–carbon distances of 2.247(3) Å (Li1–C1) and 2.125(3) Å (Li1–C1') in molecule **1** and 2.252(3) Å (Li3–C22) and 2.108(3) Å (Li3–C22') in molecule **2**. These lithium atoms display a distorted trigonal-planar environment, with angle sums of 359.6° at Li1 and 358.8° at Li3. The two additional terminal lithium atoms (Li2/Li2', Li4/Li4') in each molecule are bound to the same C_5H_4 carbon atoms (Li2 to C8, Li4 to C29), which thereby bridge the two types of Li atoms, and their coordination sphere is completed by three pmtda nitrogen atoms to afford highly distorted tetrahedral geometries. The same structural motif has been observed for the dimeric pmtda complexes $[(\eta^5\text{-C}_5\text{H}_4\text{Li})_2\text{Fe}] \cdot \text{pmdta}$ ¹⁹ and $[(\eta^5\text{-C}_5\text{H}_4\text{Li})\text{Mn}(\eta^6\text{-C}_6\text{H}_5\text{Li})] \cdot \text{pmdta}$,²⁰ and the Li–C and Li–N distances in **4** are in good agreement with the values reported for these complexes. In contrast, the

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Scheme 3. Dilithiation of Trocicene and Preparation of 1,1'-Bis(diphenylphosphanyl)trocicene (**1**)



thf complexes $[(\eta^6\text{-C}_6\text{H}_5\text{Li})_2\text{Cr}]_2 \cdot 7\text{thf}$,²¹ $[(\eta^6\text{-C}_6\text{H}_5\text{Li})_2\text{Mo}]_2 \cdot 6\text{thf}$,²² and $[(\eta^6\text{-C}_6\text{H}_5\text{Li})_2\text{V}]_2 \cdot 7\text{thf}$ ²³ exhibit more strongly distorted molecular structures.

The crystal structure of dilithiated trocrocene, $[(\eta^5\text{-C}_5\text{H}_4\text{Li})\text{Cr}(\eta^7\text{-C}_7\text{H}_6\text{Li})]_2 \cdot 8\text{thf}$, displays a closely related dimeric arrangement with the terminal Li atoms stabilized by thf coordination.^{10d} It is interesting to note, however, that this structure is inverted with regard to the positions of the Cht and Cp rings, and in contrast to **4**, the *ipso*- C_5H_4 carbon atoms adopt the bridging position in the central Li_2C_2 rhomboid. This difference is a clear indication of the different metalation behavior of the Cp and Cht ligands in trocicene and trocrocene. Whereas the chromium–carbon distances in the latter structure are very similar, the titanium–carbon distances to the seven-membered rings [2.175(2)–2.219(2) Å/2.172(2)–2.217(2) Å] are significantly shorter than those to the five-membered rings [2.292(2)–2.356(2) Å/2.295(2)–2.362(2) Å], revealing, as expected for trocicene,²⁴ a much stronger interaction between the metal center and the Cht ring.^{8,25} With regard to the position of the bridging lithium atoms in **4**, this molecular structure could be regarded as an *ansa*-Cht–Cp complex or lithia[1]trocicenophane, respectively. In contrast to other covalently linked trocicenophanes,¹¹ however, bridging of the Cht and Cp rings by lithium does not impose appreciable strain on the trocicene sandwich structure, as indicated by the angles 2.9° (molecule **1**) and 4.2° (molecule **2**) between the best planes of the five- and seven-membered rings.

To test the suitability of the dilithio complex **4** as a starting material for the preparation of functionalized trocicenes, it was further used for the preparation of the previously reported trocicenyl diphosphane dppti (**1**);¹³ addition of an ethereal solution of chlorodiphenylphosphane to a suspension of **4** in diethyl ether afforded **1** as a blue-green solid in high yield (92%, Scheme 3). Although Rausch reported a similar yield via lithiation with $n\text{BuLi}/\text{tmeda}$,^{13b} we have to conclude that, in our hands, the use of pmtda and the isolation of the intermediate **4** has proved to be clearly superior. The ^{31}P NMR spectrum of **4** exhibits two singlet resonances at 18.6 and -17.7 ppm for the $\text{C}_7\text{H}_6\text{PPh}_2$ and $\text{C}_5\text{H}_4\text{PPh}_2$ phosphorus atoms, respectively, and these values are virtually identical to those published previously.^{13b}

Monolithiation of Trocicene. As described above, monolithiation of trocicene has been reported to occur exclusively at the seven-membered ring,^{12,14} which allowed, for instance, the preparation of the monophosphane $[(\eta^7\text{-C}_7\text{H}_6\text{PPh}_2)\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**) in satisfactory yield.¹⁵ This route is fully reproducible and, in our hands, **2** was isolated in 73% yield after stirring an

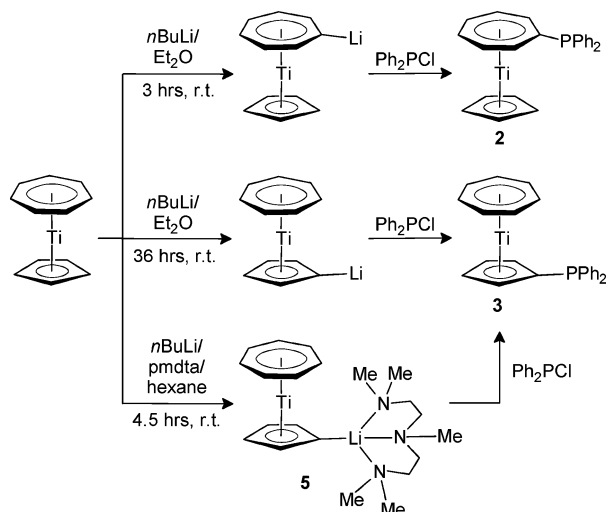
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Scheme 4. Selective Monolithiation of Tropicene and Preparation of Isomeric Mono(diphenylphosphanyl)tropicenes **2** and **3**

equimolar mixture of tropicene and *n*-BuLi/hexane in diethyl ether for 3 h at room temperature followed by addition of an ethereal solution of ClPPh₂ at $-78\text{ }^{\circ}\text{C}$ (Scheme 4). The ¹H NMR spectrum is in agreement with the previously published data.^{15b} In addition, the ³¹P NMR spectrum exhibits a singlet resonance at 18.5 ppm, which is indicative of phosphorus-substitution at the seven-membered ring.

We observed, however, that mixtures of the two regioisomers [(η^7 -C₇H₆PPh₂)Ti(η^5 -C₅H₅)] (**2**) and [(η^7 -C₇H₇)Ti(η^5 -C₅H₄PPh₂)] (**3**) were obtained if the *n*-BuLi/tropicene solution was allowed to react for prolonged periods of time, indicating that the lithiation at the five-membered ring might be thermodynamically favored. Indeed, [(η^7 -C₇H₇)Ti(η^5 -C₅H₄PPh₂)] (**3**) could be isolated as the sole product in analytically pure form in 62% yield after stirring in diethyl ether for 36 h, followed by quenching with ClPPh₂ (Scheme 4). The ³¹P NMR resonance is observed at -17.5 ppm, which is a clear indication of phosphorus-substitution at the five-membered ring. The spectroscopic data are in full agreement with those previously published for a sample of **3**, which had been prepared by the reductive method shown in Scheme 2.¹⁸ Since amines have a marked effect on the basicity of organolithium compounds²⁶ and since the use of pmtda has also been beneficial for the dilithiation of tropicene (*vide supra*), we anticipated that the thermodynamically favored lithio complex [(η^7 -C₇H₇)Ti(η^5 -C₅H₄Li)] should be conveniently accessible by reaction of tropicene with *n*-BuLi/pmdta in hexane. Consequently, a dark green pyrophoric solid was isolated in almost quantitative yield (95%) after stirring for 4.5 h at room temperature, followed by filtration and washing with hexane. Elemental analysis indicated that this material has the composition [(η^7 -C₇H₇)Ti(η^5 -C₅H₄Li)]·pmdta (**5**) and is sufficiently pure to be used directly for further transformations; it can also be stored under an inert atmosphere at room temperature for several days and was fully characterized by means of NMR spectroscopy. Thus, two characteristic pseudotriplets corresponding to the α - and β -C₅H₄ protons are observed at 6.05 and 5.67 ppm in the ¹H NMR spectrum together with a singlet resonance for the C₇H₇ hydrogen atoms at 5.61 ppm.

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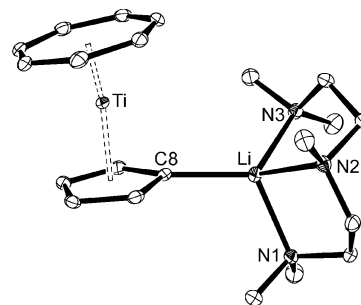


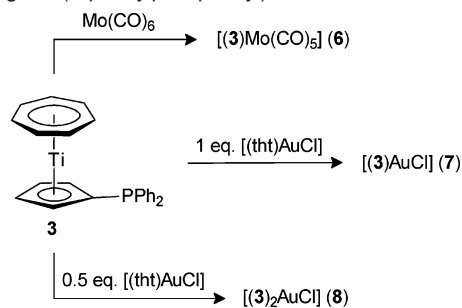
Figure 2. ORTEP view of [(η^7 -C₇H₇)Ti(η^5 -C₅H₄Li)]·pmdta (**5**). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Li–C8 2.115(3), Li–N1 2.121(3), Li–N2 2.127(3), Li–N3 2.123(3), Ti–C_{cht} 2.224(2)–2.250(2), Ti–C_{cp} 2.280(2)–2.335(2); C8–Li–N1 114.68(14), C8–Li–N2 123.76(15), C8–Li–N3 123.79(15), N1–Li–N2 85.60(12), N1–Li–N3 112.65(14), N2–Li–N3 87.95(12).

To unambiguously confirm lithium coordination at the Cp ring, an X-ray crystal structure determination was performed on single crystals of **5** that were obtained from a toluene solution at $-30\text{ }^{\circ}\text{C}$. The molecular structure of **5** is shown in Figure 2, revealing that the lithium atom is bound to the C₅H₄ ring [Li–C8 = 2.115(3) Å]. The lithium coordination sphere is completed by coordination of three pmtda nitrogen atoms to afford a highly distorted tetrahedral environment with acute N1–Li–N2 and N2–Li–N3 angles of 85.60(12) $^{\circ}$ and 87.95(12) $^{\circ}$, respectively. The orientation of the Cht and Cp ring planes deviates by 6.7 $^{\circ}$ from that expected for an ideal sandwich structure, which is presumably a result of the steric requirements of the Li(pmdta) moiety. It was calculated, however, that bending apart of the Cht and Cp rings in tropicene carries only a small energy penalty.⁸ Naturally, the convenient isolation of the pmdta complex **5** suggested that it should also be a superior starting material for the preparation of the monophosphane [(η^7 -C₇H₇)Ti(η^5 -C₅H₄PPh₂)] (**3**), and indeed, this compound was isolated in 84% yield from the reaction of ClPPh₂ with **5** in diethyl ether.

Syntheses of Tropicenyl Phosphane Metal Complexes. The availability of the tropicenyl diphosphane **1** and of the monophosphanes **2** and **3** encouraged us to prepare a few selected transition metal complexes and to compare their coordination behavior with that of ferrocenyl phosphanes. Since several transition metal complexes containing the monophosphane [(η^7 -C₇H₇PPh₂)Ti(η^5 -C₅H₅)] (**2**) are known, for example, [(**2**)M(CO)_x] (M = Ni, x = 3; M = Fe, x = 4; M = Mo, x = 5),¹⁵ we aimed at synthesizing similar complexes with its regioisomer [(η^7 -C₇H₇)Ti(η^5 -C₅H₄PPh₂)] (**3**). Thus, the reaction of **3** with Mo(CO)₆ in a boiling toluene/thf mixture afforded the molybdenum complex [(**3**)Mo(CO)₅] (**6**) as a green solid in moderate yield (Scheme 5). The strong low-field shift of the ³¹P NMR resonance from -17.5 ppm in **3** to 23.0 ppm in **6** gives a clear indication of metal-phosphane coordination. The IR spectrum exhibits four CO absorptions at 2069 (A₁⁽²⁾), 1981 (B₁), 1934 (A₁⁽¹⁾) and 1917 (E) cm⁻¹, which are similar to those recorded for [(**2**)Mo(CO)₅] (2080, 1995, 1940, and 1915 cm⁻¹).^{15b} Since the A₁⁽²⁾ CO stretching mode has been used as a qualitative indicator for comparison of the relative donor abilities of various phosphanes,²⁷ it can be concluded that the phosphane **3** is a better donor than its regioisomer **2**. Complex **6** was additionally characterized by X-ray diffraction analysis, and the molecular

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Scheme 5. Preparation of Molybdenum and Gold(I) Complexes Containing the (Diphenylphosphanyl)troticene **3**^a



^a tht = tetrahydrothiophene.

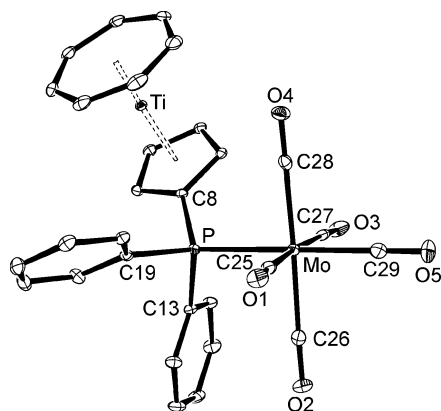


Figure 3. ORTEP view of [(3)Mo(CO)₅] (**6**). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–P 2.5423(4), Mo–C25 2.0397(15), Mo–C26 2.0542(14), Mo–C27 2.0548(15), Mo–C28 2.0428(14), Mo–C29 2.0113(16), Ti–C_{ChT} 2.1984(15)–2.2100(14), Ti–C_{Cp} 2.3337(13)–2.3428(12), P–C8 1.8154(13); P–Mo–C25 98.02(4), P–Mo–C26 89.46(4), P–Mo–C27 86.06(4), P–Mo–C28 90.27(4), P–Mo–C29 175.50(5).

structure is shown in Figure 3. The Mo atom resides in a slightly distorted octahedral environment, while the titanium atom displays only a small deviation from an ideal sandwich structure with a dihedral Cht–Cp angle of 4.1°. The Mo–P bond of 2.5423(4) Å is shorter than that determined for [(2)Mo(CO)₅] (2.563(2) Å),^{15b} further corroborating the slightly stronger donor ability of **3**. Both Mo–P distances fall in the range observed for other Mo(CO)₅ complexes containing related metallo phosphane ligands.²⁸

The monophosphane **3** was additionally employed in the preparation of gold(I) complexes, since numerous Au(I) complexes containing analogous ferrocenyl phosphane ligands have been prepared and structurally characterized.^{29,30} The reaction of **3** with 1 equiv of the Au(I) precursor compound [(tht)AuCl] (tht = tetrahydrothiophene) led to the formation of a green solid

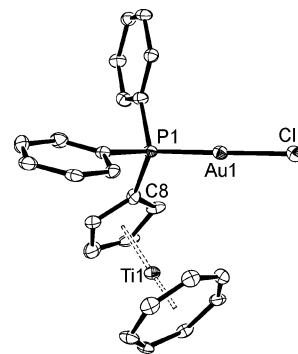


Figure 4. ORTEP view of one independent molecule of [(3)AuCl] (**7**). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] in molecule 1: Au1–P1 2.216(3), Au1–Cl1 2.287(3), Ti1–C_{ChT} 2.178(13)–2.211(12), Ti1–C_{Cp} 2.287(14)–2.327(13); P1–Au1–Cl1 178.60(18). Molecule 2: Au2–P2 2.219(3), Au2–Cl2 2.302(3), Ti2–C_{ChT} 2.189(13)–2.218(13), Ti2–C_{Cp} 2.320(11)–2.376(14); P2–Au2–Cl2 178.63(15).

with the composition [(3)AuCl] (**7**). As also observed for the Mo complex **6**, phosphane coordination effects a pronounced downfield shift of the ³¹P NMR resonance, which is observed at 21.5 ppm. Complex **7** crystallizes in the space group *P*2₁ with two independent molecules and two thf molecules in the asymmetric unit, and Figure 4 shows molecule 1 as a representative of the two structurally closely related molecules. As expected for Au(I) compounds, **7** displays a linear P–Au–Cl axis³¹ with angles P1–Au1–Cl1 = 178.60(18)° (molecule 1) and P2–Au2–Cl2 = 178.63(15)° (molecule 2). The P–Au [2.216(3)/2.219(3) Å] and Au–Cl [2.287(3)/2.302(3) Å] distances in **7** are similar to those previously determined for gold(I) chloride complexes containing (diphenylphosphanyl)ferrocene ligands.²⁹

Treatment of the gold(I) precursor [(tht)AuCl] with 2 equiv of **3** afforded the 2:1 complex [(3)₂AuCl] (**8**) as a turquoise solid in good yield. The ³¹P NMR spectrum exhibits a single resonance at 19.5 ppm (in CD₂Cl₂), indicating the presence of two identical phosphorus nuclei. The molecular structure of **8** was established by X-ray diffraction analysis (Figure 5). The molecule displays crystallographic C₂ symmetry with the Au and Cl atoms lying on the C₂ axis. Accordingly, the gold(I) atom is in a perfectly planar environment; nevertheless, its coordination sphere is strongly distorted from ideal trigonal planarity, since the P–Au–P' angle [139.08(5)°] is significantly larger than the P–Au–Cl/P'–Au–Cl angles [110.46(2)°]. The Au–P and Au–Cl distances are 2.3167(9) Å and 2.5656(14) Å, which is appreciably longer than the corresponding distances in the monophosphane complex **7**. This elongation is in agreement with the trend observed for other three-coordinated gold(I) complexes,³² including related P₂AuCl complexes containing ferrocenyl phosphane ligands.³⁰

For comparison of the ligand properties of the various troticenyl mono- and diphosphanes, we aimed at the preparation of a series of complexes in which **1**–**3** are coordinated to the same complex fragment. The PtCl₂ fragment was chosen, since

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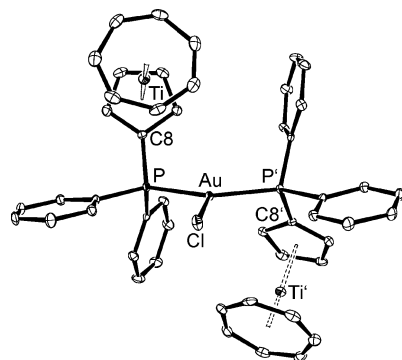


Figure 5. ORTEP view of $[(3)_2\text{AuCl}]$ (**8**). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: Au–P 2.3167(9), Au–Cl 2.5656(14), Ti–C_{Ch} 2.184(4)–2.219(4), Ti–C_{Cp} 2.334(3)–2.377(4); P–Au–P' 139.08(5), P–Au–Cl 110.46(2).

numerous square-planar platinum(II) dichloride complexes containing ferrocenyl phosphane ligands have been studied. In particular, platinum complexes of 1,1'-bis(diphenylphosphanyl)-ferrocene, $[(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}]$ (dppf), have been studied extensively in the past, and the dichloride $[(\text{dppf})\text{PtCl}_2]$ has found diverse applications, for example, in homogeneous catalysis³³ and materials science,³⁴ and has also been used for the construction of supramolecular architectures³⁵ and heteropolymetallic arrays³⁶ and for the stabilization of numerous ligand systems such as sulfur- or selenium-containing ligands,³⁷ carboxylate ligands,³⁸ and hydridic species.³⁹ In addition, ligand exchange reactions at the (dppf)Pt moiety have been widely studied, with particular emphasis on the interaction with ligands

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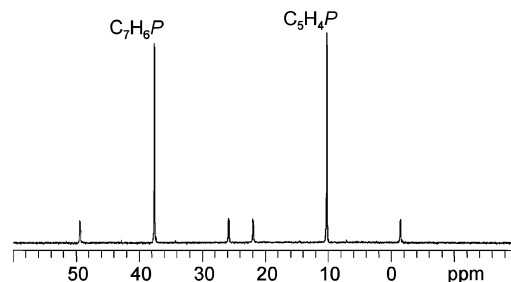
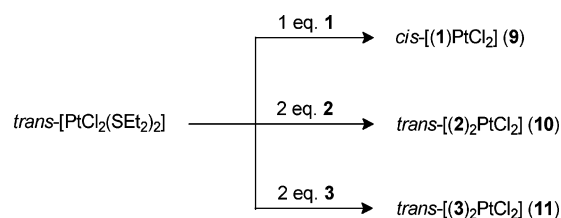


Figure 6. ^{31}P NMR spectrum of **9** in CD_2Cl_2 ; the satellites are due to ^{31}P – ^{195}Pt coupling, whereas the ^{31}P – ^{31}P coupling is not resolved in this presentation.

Scheme 6. Preparation of Platinum(II) Complexes Containing the Tropicene-Phosphane Ligands **1**, **2**, and **3**



of bioinorganic or medicinal relevance.⁴⁰ The analogous titanium–platinum complex *cis*- $[(1)\text{PtCl}_2]$ (**9**) was prepared in high yield by the reaction of *dppti* (**1**) with *trans*- $[\text{PtCl}_2(\text{SEt}_2)_2]$ ⁴¹ (Scheme 6). In agreement with the presence of two different phosphorus nuclei, the ^{31}P NMR spectrum of **9** displays two doublets at 38.4 ($\text{C}_7\text{H}_6\text{PPh}_2$) and 10.5 ppm ($\text{C}_5\text{H}_4\text{PPh}_2$) with a $^2J(^{31}\text{P}$ – $^{31}\text{P})$ coupling constant of 13.4 Hz (Figure 6). Furthermore, these resonances show large ^{31}P – ^{195}Pt couplings of 3812 and 3780 Hz, respectively, which is in agreement with the $^1J(^{31}\text{P}$ – $^{195}\text{Pt})$ coupling constant reported for $[(\text{dppf})\text{PtCl}_2]$ (3778 Hz),⁴² although a lower range (3480–3680 Hz) has been ascribed to *cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$ complexes.⁴³

The molecular structure of **9** was also established by X-ray diffraction analysis (Figure 7), confirming the *cis*-configuration of the P_2PtCl_2 moiety. The Pt atom resides in a square-planar environment with a P1–Pt–P2 bite angle of $98.02(5)^\circ$, which is slightly smaller than the corresponding angles reported for the X-ray crystal structures of $[(\text{dppf})\text{PtCl}_2]$ (99.0°),⁴²

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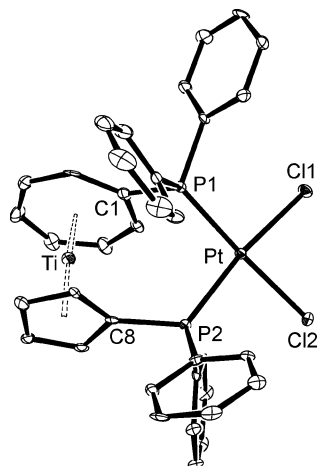


Figure 7. ORTEP view of [(1)PtCl₂] (**9**). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt–P1 2.2507(15), Pt–P2 2.2672(15), Pt–Cl1 2.3506(13), Pt–Cl2 2.3433(15), Ti–C_{Ch} 2.153(5)–2.218(6), Ti–C_{Cp} 2.293(5)–2.315(5); P1–Pt–P2 98.02(5), P1–Pt–Cl1 90.51(5), P2–Pt–Cl2 84.81(5), Cl1–Pt–Cl2 86.90(5).

[(dppf)PtCl₂]·CHCl₃ (99.3°),⁴⁴ and [(dppf)PtCl₂]·0.5acetone (99.3°).⁴⁵ The Pt–P bond distances in **9** are also very similar to those reported for the dppf analogue, with the Pt–P1 bond [2.2507(15) Å] being somewhat shorter than Pt–P2 [2.2672(15) Å]; this correlates with the slightly larger ³¹P–¹⁹⁵Pt coupling constant determined for the C₇H₆PPh₂ phosphorus atom (*vide supra*). It should be noted that complex **9** can be regarded as a [3]troticene with a P1–Pt–P2 bridge between the seven- and five-membered rings; this three-atom bridge, however, does not impose considerable strain, and the angle between the Cht and Cp ring planes of 8.0° indicates only a relatively small deviation from an unstrained sandwich structure.⁸

The reaction of *trans*-[PtCl₂(SET₂)₂] with 2 equiv of the monophosphanes **2** and **3** afforded the complexes *trans*-[(2)₂PtCl₂] (**10**) and *trans*-[(3)₂PtCl₂] (**11**) as green solids in good yield. The *trans*-orientation of the phosphane ligands can be assigned by ³¹P NMR spectroscopy, since the phosphorus resonances of **10** (31.5 ppm) and **11** (6.7 ppm) show ³¹P–¹⁹⁵Pt couplings of 2652 and 2634 Hz, respectively, that are significantly smaller than those in the *cis*-configured complex **9** and fall in the range ascribed to *trans*-[PtCl₂(PR₃)₂] complexes.^{42,43} Single crystals of **10**·3CH₂Cl₂ and **11**·2CH₂Cl₂ were subjected to X-ray diffraction analyses, and the resulting molecular structures exhibit the expected *trans*-configuration (Figure 8). Both molecules display crystallographic inversion symmetry, rendering the platinum environment perfectly planar with linear P–Pt–P' and Cl–Pt–Cl' axes. The P–Pt–Cl and P–Pt–Cl' angles in **10** and **11** are 92.67(4)/87.33(4)° and 92.87(3)/87.13(3)°, respectively, revealing in both cases a slight distortion from a perfectly square toward a rhomboid geometry. Interestingly, the same crystallographic inversion symmetry was observed for *trans*-P₂PtCl₂ complexes containing the related (diphenylphosphanyl)ferrocene ligand, [(η⁵-C₅H₅)Fe(η⁵-C₅H₄-PPh₂)]₂,⁴⁶ or functionalized systems such as [(η⁵-C₅H₄OMe)-

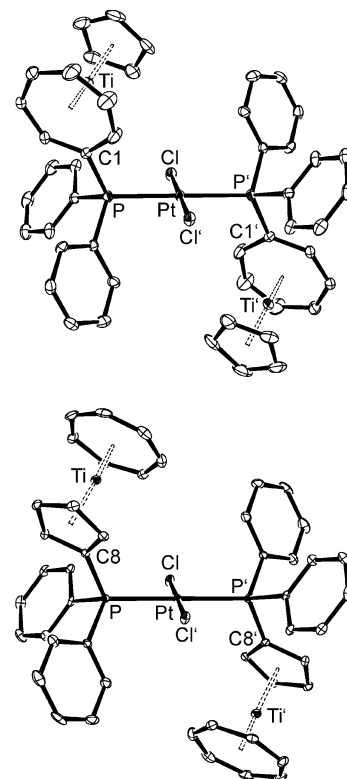


Figure 8. ORTEP views of [(2)₂PtCl₂] (**10**, top) and [(3)₂PtCl₂] (**11**, bottom). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **10**: Pt–P 2.3386(9), Pt–Cl 2.3130(10), Ti–C_{Ch} 2.181(5)–2.220(4), Ti–C_{Cp} 2.300(5)–2.321(5); P–Pt–Cl 92.67(4), P–Pt–Cl' 87.33(4). **11**: Pt–P 2.3215(8), Pt–Cl 2.3042(7), Ti–C_{Ch} 2.199(4)–2.223(3), Ti–C_{Cp} 2.332(3)–2.340(3); P–Pt–Cl 92.87(3), P–Pt–Cl' 87.13(3).

Fe(η⁵-C₅H₄PPh₂)]⁴⁷ and [(η⁵-C₅H₅CO₂H)Fe(η⁵-C₅H₄PPh₂)]₂.⁴⁸ The Pt–P and Pt–Cl bond lengths in **10** and **11** also fall in the ranges found for these ferrocene analogs.

Conclusion

Although the first reports on the lithiation of [(η⁷-C₇H₇)Ti(η⁵-C₅H₅)] (troticene) appeared more than 30 years ago, our present contribution demonstrates for the first time that selective mono- and dilithiation of this 16-electron sandwich molecule can be conveniently achieved. Whereas the previously observed monolithiation at the Cht ring is apparently kinetically controlled, the formation of the thermodynamically favored Cp-metalated lithiotroticene is observed after prolonged reaction times; better yet, this species is conveniently accessible by using a combination of *n*-BuLi and the triamine pmdta. Accordingly, selective functionalization of troticene is possible, which has been demonstrated by the syntheses of the troticenylium mono- and diphosphanes **1**–**3**. It should be noted that the transition metal complexes derived from these phosphanes do not display any secondary interactions involving the titanium atom, a situation that is different from the reactivity of analogous zirconium- or hafnium-based sandwich complexes.^{8,18,49,50} Therefore, tro-

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Table 1. Crystallographic Data

	4 · toluene	5	6	7 · THF	8	9	10 · 3CH ₂ Cl ₂	11 · 2CH ₂ Cl ₂
Empirical formula	C ₄₉ H ₇₄ Li ₄ N ₆ Ti ₂	C ₂₁ H ₃₄ LiN ₃ Ti	C ₂₉ H ₂₁ MoO ₅ PTi	C ₂₈ H ₂₉ AuClO ₄ PTi	C ₄₈ H ₄₂ AuClP ₂ Ti ₂	C ₃₆ H ₃₀ Cl ₂ P ₂ PtTi	C ₅₁ H ₄₈ Cl ₈ P ₂ PtTi ₂	C ₅₀ H ₄₆ Cl ₆ P ₂ PtTi ₂
<i>a</i> (Å)	12.0047(4)	20.9957(4)	31.9896(4)	10.2073(2)	25.8727(10)	10.3864(14)	11.4048(3)	10.0746(6)
<i>b</i> (Å)	12.0319(4)	7.9976(2)	10.0260(10)	13.3413(2)	8.2464(2)	13.1253(2)	15.3408(4)	10.5051(10)
<i>c</i> (Å)	17.3320(6)	12.6211(2)	17.1398(2)	18.5216(4)	20.6849(8)	22.9240(3)	14.5731(5)	12.4587(8)
α (deg)	90.282(2)	90	90	90	90	90	90	114.280(8)
β (deg)	94.171(4)	90	107.5819(12)	91.036(2)	118.242(4)	90	98.262(3)	92.360(6)
γ (deg)	101.030(2)	90	90	90	90	90	90	103.396(6)
<i>V</i> (Å ³)	2450.22(14)	2119.27(7)	5240.45(10)	2521.83(8)	3887.9(2)	3125.13(8)	2523.23(13)	1155.30(15)
<i>Z</i>	2	4	8	4	4	4	2	1
formula weight	870.70	383.35	624.27	692.80	1008.97	838.43	1297.32	1212.40
space group	<i>P</i> $\bar{1}$	<i>Pna</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>T</i> (°C)	−173	−173	−173	−173	−173	−173	−173	−173
λ (Å)	0.71073	1.54184	0.71073	1.54184	0.71073	0.71073	0.71073	0.71073
<i>D</i> _{calcd} (g cm ^{−3})	1.180	1.201	1.582	1.825	1.724	1.782	1.708	1.743
μ (mm ^{−1})	0.364	3.461	0.882	15.189	4.352	5.026	3.597	3.810
<i>R</i> (<i>F</i> _o)	0.0331	0.0272	0.0208	0.0606	0.0261	0.0299	0.0303	0.0242
<i>R</i> _w (<i>F</i> _o ²)	0.0537	0.0731	0.0429	0.1495	0.0531	0.0337	0.0547	0.0394

tropicene, which is moderately air-stable in the solid-state, can be regarded as an asymmetric analogue of ferrocene, and in view of the ubiquity of ferrocene derivatives in the chemical sciences, the potential for the development of an equally rich chemistry based on the selective functionalization of tropicene can be envisaged.

Experimental Section

General Procedures. All operations were performed in a glovebox in a dry argon atmosphere (MBraun 200B) or on a high-vacuum line using Schlenk technique. Commercial grade solvents were purified by a solvent purification system from MBraun GmbH and stored over molecular sieves (4 Å) prior to their use. Tropicene,^{15b} *trans*-Pt(SEt₂)Cl₂⁴¹ and (tht)AuCl⁵¹ were synthesized according to previous methodology reported in the literature. *n*-Butyllithium (1.6 M in Hexane, Aldrich) and Mo(CO)₆ (Aldrich) were used as received. *N,N',N'',N''',N''''*-pentamethyldiethylenetriamine (Aldrich) was purified by distillation over CaH₂. Chlorodiphenylphosphane (Aldrich) was distilled under high vacuum. Elemental analysis (C, H, N) was performed by combustion and gas chromatographical analysis with an Elementar Vario MICRO elemental analyzer. The ¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker DPX 200 (200 MHz), Bruker AV 300 (300 MHz), Bruker DRX 400 (400 MHz) and Bruker AVII 600 (600 MHz) devices. The chemical shifts are expressed in parts per million (ppm) with tetramethylsilane (TMS) as an internal standard. Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), vq (virtual quartet), m (multiplet), sept (septet), and br (broad). The reactions involving gold were performed under exclusion of light.

Synthesis of [(η^7 -C₇H₆Li)Ti(η^5 -C₅H₄Li)]·pmdta (4). A slurry of tropicene (1.53 g, 7.50 mmol) was suspended in hexane (20 mL) at room temperature. In an additional flask, a solution of the lithiating agent was prepared by the addition of *n*-butyllithium (1.6 M, 18.75 mmol) and pmdta (3.9 mL, 18.75 mmol) in 10 mL of hexane. The resulting mixture was stirred for 10 min and was then slowly added to the above suspension of tropicene via a dropping funnel. The reaction, which gradually changed from blue slurry to a dark-green suspension, was allowed to stir overnight. The solid was isolated by filtration, followed by repeated washing with hexane. The product was thoroughly dried under high vacuum, affording a green pyrophoric solid in high yield (2.48 g, 86%). The solid can be stored for several days under an inert atmosphere at room temperature. X-ray quality crystals could be obtained by cooling a saturated solution of **4** in toluene to −30 °C. Elemental analysis (%) calcd for C₂₁H₃₃Li₂N₃Ti: C, 64.79; H, 8.54; N, 10.79. Found: C, 64.32; H, 8.66; N, 11.37. ¹H NMR (200 MHz, toluene-

*d*₆): δ 6.24 (m br, 2H, C₇H₆), 5.99 (m br, 2H, C₇H₆), 5.89 (m br, 4H, C₅H₄), 5.62 (m br, 2H, C₇H₆), 2.00–1.76 (br, 23H, pmdta).

Synthesis of [(η^7 -C₇H₇)Ti(η^5 -C₅H₄Li)]·pmdta (5). A suspension of tropicene (0.5 g, 2.45 mmol) was prepared in 15 mL of hexane at room temperature. In an additional flask, a solution of lithiating agent was made from *n*-butyllithium (1.6 M, 2.57 mmol), pmdta (0.54 mL, 2.57 mmol) in 7 mL of hexane. Then, the lithiating mixture was stirred for 10 min and then slowly added to the original suspension of tropicene. The solution was stirred for 4.5 h, at which time the blue solution had completely changed into a dark green suspension. The solid was filtered off and washed repeatedly with hexane. Drying under high vacuum yielded a dark green pyrophoric crystalline solid (0.89, 95% yield). The solid can be stored for several days under an inert atmosphere at room temperature. Suitable crystals for X-ray analysis were obtained by cooling a saturated solution of **5**·pmdta in toluene to −30 °C. Elemental analysis (%) calcd for C₂₁H₃₄LiN₃Ti: C, 65.80; H, 8.94; N, 10.96. Found: C, 65.28; H, 8.85; N, 11.10. ¹H NMR (600 MHz, benzene-*d*₆): δ 6.05 (t, 2H C₅H₄), 5.67 (t, 2H, C₅H₄), 5.61 (s, 7H, C₇H₇), 1.92–1.64 (br, 23H, pmdta). ¹³C{¹H} NMR (150.9 MHz, benzene-*d*₆): δ 128.9 (s, *i*-C₅H₄), 112.0 (s, α -C₅H₄), 101.3 (s, β -C₅H₄), 83.5 (s, C₇H₇), 57.7 (s, CH₂NMe₂), 53.9 (s, CH₂NMe), 46.2 (s, N(CH₃)₂), 45.3 (s, NCH₃).

Synthesis of [(η^7 -C₇H₆PPh₂)Ti(η^5 -C₅H₄PPh₂)] (1). A suspension of dilithiotropicene **4** (0.6 g, 1.53 mmol) was prepared in 15 mL of diethyl ether and the reaction vessel was chilled to −78 °C. A solution of diphenylchlorophosphane (0.6 mL, 3.3 mmol) in diethyl ether (7 mL) was slowly added via a dropping funnel to the above reaction mixture, which was then allowed to warm slowly to room temperature and was stirred overnight. At this time, a blue-green suspension was obtained. All volatiles were removed under vacuum and the residue was extracted in hot toluene and filtered through Celite. The solvent was evaporated and the crude solid was washed with hexane to remove excess of diphenylchlorophosphane. Drying the solid afforded a light blue-green solid **2** in high yield (0.810 g, 92% yield). Elemental analysis (%) calcd for C₃₆H₃₀P₂Ti: C, 75.53; H, 5.28. Found: C, 74.36; H, 5.55. ¹H NMR (200 MHz, benzene-*d*₆): δ 7.49 – 6.99 (m, 20H, PC₆H₅), 5.80 (t, 2H C₇H₆), 5.42 (m, 4H, C₇H₆), 5.05 (m, 4H, C₅H₄). ¹³C{¹H} NMR (50.3 MHz, benzene-*d*₆): δ 141.4 (d, ¹*J*_{C-P} = 14.3 Hz, *i*-C₆H₅), 140.4 (d, ¹*J*_{C-P} = 12.5 Hz, *i*-C₆H₅), 134.7 (d, ²*J*_{C-P} = 20.1 Hz, *o*-C₆H₅), 134.5 (d, ²*J*_{C-P} = 20.2 Hz, *o*-C₆H₅) 133.4 (m, *p*-C₆H₅), 132.0 (m, *p*-C₆H₅), 129.5 (m, *m*-C₆H₅), 128.9 (m, *m*-C₆H₅), 111.0 (d, ¹*J*_{C-P} = 10.2 Hz, *i*-C₅H₄), 104.7 (d, ²*J*_{C-P} = 13.5 Hz, α -C₅H₄), 101.9 (d, ³*J*_{C-P} = 13.5 Hz, β -C₅H₄), 95.1 (d, ¹*J*_{C-P} = 10.8 Hz, *i*-C₇H₆), 94.2 (d, ²*J*_{C-P} = 26.3 Hz, α -C₅H₄), 89.9 (d, ³*J*_{C-P} = 8.7 Hz, β -C₅H₄), 89.1 (m, γ -C₇H₆). ³¹P{¹H} NMR (81 MHz, benzene-*d*₆): δ 18.6 (s, C₇H₆PPh₂), −17.7 (s, C₅H₄PPh₂).

Synthesis of [(η^7 -C₇H₆PPh₂)Ti(η^5 -C₅H₅)] (2). Compound **2** was synthesized according to a modification of the procedure outlined

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by Dixneuf et al.^{15b} To a blue suspension of troiticene (0.475 mg, 2.32 mmol) in 20 mL of diethyl ether, 0.157 mL of 1.6 M *n*-butyllithium (2.51 mmol) in hexane was added slowly via a syringe at room temperature and the mixture was stirred for 3 h at room temperature. During the reaction, the blue suspension gradually changed into a dark green solution. The resulting solution was cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of diphenylchlorophosphane (0.481 mL, 2.68 mmol) in 5 mL of diethyl ether was slowly added via a dropping funnel. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. All the volatiles were evaporated under vacuum and the residue was extracted with toluene and dried under vacuum. The green solid was washed with hexane and dried under high vacuum affording 662 mg of **1** (73% yield). ¹H NMR (200 MHz, benzene-*d*₆): δ 7.53–7.02 (m, 10H, PC₆H₅), 5.82 (m, 2H C₇H₆), 5.41 (m, 4H, C₇H₆), 4.82 (s, 5H, C₅H₄). ³¹P{¹H}NMR (81 MHz, benzene-*d*₆): δ 18.5 (s, C₇H₆PPh₂). These values are in agreement with those reported previously.^{15b}

Synthesis of [(η^7 -C₇H₇)/Ti(η^5 -C₅H₄PPh₂)] (3). A solution chlorodiphenylphosphane (0.2 mL, 1.1 mmol) in diethyl ether (5 mL) was added slowly to a suspension of monolithiotroticene **5** (0.35 g, 0.91 mmol) in 20 mL of hexane at $-78\text{ }^{\circ}\text{C}$. The mixture was warmed to room temperature and stirred overnight, whereby it slowly changed from a green suspension to a light green solution. The filtrate was dried under vacuum and the solid was washed with two small portions of cold hexane (2 \times 3 mL). The residue was dried under vacuum affording a light green solid (0.29 mg, 84% yield). ¹H NMR (200 MHz, chloroform-*d*₁): δ 7.36–7.11 (m, 10H, PC₆H₅), 5.44 (s, 7H C₇H₇), 5.37 (t, 2H, C₅H₄), 5.15 (t, 2H, C₅H₄). ¹³C{¹H} NMR (50.3 MHz, chloroform-*d*₁): δ 139.4 (d, ¹J_{C-P} = 10.4 Hz, *i*-C₆H₅), 133.7 (d, ²J_{C-P} = 20.1 Hz, *o*-C₆H₅), 128.9 (s, *p*-C₆H₅), 128.4 (d, ²J_{C-P} = 6.8 Hz, *m*-C₆H₅), 108.4 (d, ¹J_{C-P} = 9.5 Hz, *i*-C₅H₄), 102.7 (d, ²J_{C-P} = 13.7 Hz, α -C₅H₄), 99.9 (d, ³J_{C-P} = 4.0 Hz, β -C₅H₄), 87.2 (s, C₇H₆). ³¹P{¹H} NMR (81 MHz, chloroform-*d*₁): δ -17.5 (s, C₅H₄PPh₂). Full analytical data of this compound were published recently.¹⁸

Synthesis of [(3)Mo(CO)₅] (6). A total of 200 mg (0.52 mmol) of **3** and 1 equiv (136 mg, 0.52 mmol) of [Mo(CO)₆] were placed in a Schlenk tube with 15 mL of toluene and 5 mL of thf. The reaction mixture was heated to reflux for 2 h. After filtration through a plug of Celite, the solvent was removed in high vacuum. The green residue was washed with hexane and dried in high vacuum, yielding 82 mg (0.13 mmol, 24%) of **6**. Suitable crystals for X-ray diffraction analysis were obtained by cooling a saturated thf solution of **6** to $-30\text{ }^{\circ}\text{C}$. Anal. Calcd for C₂₉H₂₁MoO₅PtI: C, 55.80; H, 3.39. Found: C, 56.81; H, 3.66. ¹H NMR (200 MHz, benzene-*d*₆): δ 7.45 (m, 4H, *o*-C₆H₅); 7.05 (m, 6H, C₆H₅); 5.40 (s, 7H, C₇H₇); 5.41 (m, 2H, β -C₅H₄), 5.12 (m, 2H, α -C₅H₄). ¹³C{¹H} NMR (50 MHz, benzene-*d*₆): δ 206.8 (s, CO), 206.6 (s, CO), 139.9 (d, ¹J_{C-P} = 38.3 Hz, *i*-C₆H₅), 133.1 (d, ²J_{C-P} = 12.6 Hz, *o*-C₆H₅), 130.8 (s, *p*-C₆H₅), 128.8 (d, ³J_{C-P} = 1.5 Hz, *m*-C₆H₅), 108.0 (d, ¹J_{C-P} = 37.5 Hz, *i*-C₅H₄), 104.5 (d, ²J_{C-P} = 11.4 Hz, α -C₅H₄), 100.5 (³J_{C-P} = 7.6 Hz, β -C₅H₄), 88.4 (s, C₇H₇). ³¹P{¹H} NMR (81 MHz, benzene-*d*₆): δ 23.0 (s, PPh₂). IR(ATR): 2069, 1981, 1934, 1917 cm⁻¹ (*v* (CO)).

Synthesis of [(3)AuCl] (7). A total of 165 mg (0.51 mmol) of [(tht)AuCl] was dissolved in the least amount of CH₂Cl₂ and cooled to $-78\text{ }^{\circ}\text{C}$. One equivalent of **3** (200 mg, 0.56 mmol) was dissolved in 10 mL of CH₂Cl₂, transferred into a dropping funnel, cooled to $-30\text{ }^{\circ}\text{C}$ and slowly added to the Au(I) solution. The reaction mixture was allowed to warm to room temperature overnight and filtered through a plug of Celite followed by removal of the solvent. The green, oily residue was washed with hexane until it became a green solid. Compound **7** was obtained in moderate yields (97 mg, 0.16 mmol, 31%) and a suitable crystal for X-ray diffraction analysis was obtained by slow diffusion of pentane into a saturated solution of **7** in thf at $-30\text{ }^{\circ}\text{C}$. Anal. Calcd for C₂₄H₂₁AuClPtI: C, 46.44; H 3.41. Found: C, 47.07; H, 3.89. ¹H NMR (200 MHz, benzene-*d*₆): δ 7.21 (m, 4H, *o*-C₆H₅), 6.87 (br m, 6H, C₆H₅), 5.46 (s, 7H, C₇H₇), 4.86 (m, 4H, C₅H₄). ¹³C (100 MHz, dichloromethane-*d*₂): δ

131.6 (br, *m*-C₆H₅), 131.2 (br, *p*-C₆H₅), 128.9 (br, *o*-C₆H₅), 103.4 (α -C₅H₄), 101.2 (β -C₅H₄), 88.5 (C₇H₇). ³¹P{¹H} NMR (81 MHz, benzene-*d*₆): δ 21.5 (s, PPh₂).

Synthesis of [(3)₂AuCl] (8). A total of 100 mg (0.26 mmol) of **3** was dissolved in 10 mL of thf and cooled to $-30\text{ }^{\circ}\text{C}$. Over a period of 30 min, this solution was added dropwise to a solution of 41 mg (0.13 mmol) of [(tht)AuCl] and dissolved in 5 mL of thf, at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to warm gradually to room temperature and filtered through a plug of Celite. The solvent was removed in high vacuum and the greyish-green residue was extracted with CH₂Cl₂, filtered and dried, giving **8** as a turquoise solid in good yields (83 mg, 0.08 mmol, 62%). ¹H NMR (400 MHz, dichloromethane-*d*₂): δ 6.57 (m, 8H, *o*-C₆H₅), 6.17 (m, 10H, C₆H₅), 5.55 (br, 4H, α -C₅H₄), 5.50 (s, 14H, C₇H₇), 5.41 (br, 4H, β -C₅H₄). ¹³C{¹H} NMR (100 MHz, dichloromethane-*d*₂): δ 133.9 (d, ¹J_{CP} = 11.8 Hz, *i*-C₆H₅), 131.7 (br, *m*-C₆H₅), 131.2 (br, *p*-C₆H₅), 129.2 (d, ²J_{CP} = 9.8 Hz, *o*-C₆H₅), 103.2 (br, α -C₅H₄), 101.3 (br, β -C₅H₄), 88.3 (s, C₇H₇). ³¹P{¹H} NMR (121 MHz, dichloromethane-*d*₂) δ 19.5 (br, PPh₂).

Synthesis of cis-[(1)PtCl₂] (9). To a dichloromethane (10 mL) solution of **1** (141 mg, 0.246 mmol) was added a solution of *trans*-Pt(SEt₂)₂Cl₂ (110 mg, 0.246 mmol) in 5 mL of dichloromethane via syringe at room temperature. The solution, which gradually changed from a light blue-green to green color, was allowed to stir overnight. The solvent was removed under reduced pressure and the residue was washed with toluene and then with hexane. Drying under vacuum afforded a green solid (180 mg, 87% yield). Suitable crystals for X-ray analysis could be obtained by slow diffusion of hexane into a dichloromethane solution of **9** at $-30\text{ }^{\circ}\text{C}$. Elemental analysis (%) calcd for C₃₆H₃₀C₁₂P₂PtTi: C, 51.57; H, 3.61. Found: C, 51.93; H, 3.84. ¹H NMR (400 MHz, dichloromethane-*d*₂): δ 7.85–7.13 (m, 20H, P(C₆H₅)₂), 5.91 (m, 2H, α H₆), 5.81 (m, 2H, β -C₇H₆), 5.62 (m, 2H, γ -C₇H₆), 5.16 (m, 2H, β -C₅H₄), 4.87 (m, 2H, α -C₅H₄). ¹³C{¹H} NMR (100 MHz, dichloromethane-*d*₂): δ 136.2 (d, ²J_{C-P} = 10.9 Hz, *o*-C₆H₅), 134.8 (d, ²J_{C-P} = 10.9 Hz, *o*-C₆H₅), 131.6 (¹J_{C-P} = 65.0 Hz, *i*-C₆H₅), 131.4 (d, ⁴J_{C-P} = 2.3 Hz, *p*-C₆H₅), 131.3 (¹J_{C-P} = 67.3 Hz, *i*-C₆H₅), 131.2 (d, ⁴J_{C-P} = 2.3 Hz, *p*-C₆H₅), 128.2 (d, ³J_{C-P} = 12.0 Hz, *m*-C₆H₅), 127.8 (d, ³J_{C-P} = 11.6 Hz, *m*-C₆H₅), 104.8 (d, ²J_{C-P} = 9.3 Hz, α -C₅H₄), 102.5 (d, ²J_{C-P} = 7.9 Hz, β -C₅H₄), 93.3 (d, ¹J_{C-P} = 14.2 Hz, β -C₇H₆), 90.5 (s, γ -C₇H₆), 89.7 (d, ¹J_{C-P} = 13.8 Hz, α -C₇H₆). ³¹P{¹H} NMR (162 MHz, dichloromethane-*d*₂): δ 38.3 (m, ²J_{P-P} = 13.4 Hz, ¹J_{P-Pt} = 3812 Hz, C₇H₆PPh₂), 10.5 (d, ²J_{P-P} = 13.4 Hz, C₅H₄PPh₂, ¹J_{P-Pt} = 3780 Hz).

Synthesis of trans-[(2)₂PtCl₂] (10). A solution of **2** (135 mg, 0.347 mmol) dissolved in 10 mL of dichloromethane was added dropwise to a solution of *trans*-Pt(SEt₂)₂Cl₂ (76.5 mg, 0.171 mmol) in dichloromethane (5 mL). The reaction mixture was allowed to stir overnight at room temperature, during which time a light blue-green solid precipitated out. The supernatant liquid was decanted from the green solid. Drying the residue under vacuum afforded light green solid **10** (147 mg, 81% yield). Suitable crystals for X-ray analysis could be obtained by cooling a saturated solution of **10** in dichloromethane to $-30\text{ }^{\circ}\text{C}$. Elemental analysis (%) calcd for C₄₈H₄₂C₁₂P₂PtTi: C, 55.30; H, 4.06. Found: C, 54.57; H, 4.25. ¹H NMR (600 MHz, dichloromethane-*d*₂): δ 7.90–7.12 (m, 10H, P(C₆H₅)₄), 5.89 (m, 2H, C₇H₆), 5.70 (m, 4H, C₇H₆), 5.43 (s, 5H, C₅H₅). ¹³C{¹H} NMR (150.9 MHz, dichloromethane-*d*₂): δ 135.3 (m, *i*-C₆H₅), 129.3 (m, *o*-C₆H₅), 128.5 (m, *p*-C₆H₅), 125.6 (m, *m*-C₆H₅), 101.8 (m, γ -C₇H₆), 100.4 (s, C₅H₅), 99.9 (m, β -C₇H₆), 98.8 (m, α -C₇H₆), 87.1 (m, *i*-C₇H₆). ³¹P{¹H} NMR (81 MHz, dichloromethane-*d*₂): δ 31.4 (s, PPh₂C₇, ¹J_{Pt-P} = 2652 Hz).

Synthesis of trans-[(3)₂PtCl₂] (11). A solution of **3** (120.3 mg, 0.310 mmol) dissolved in 10 mL of toluene was added dropwise to a solution of *trans*-Pt(SEt₂)₂Cl₂ (69 mg, 0.154 mmol) in toluene (5 mL). The reaction mixture was allowed to stir for 5 h at room temperature, during which time a dark green suspension had formed. The solvent was dried under reduced pressure and the residue was dissolved in dichloromethane and kept at $-30\text{ }^{\circ}\text{C}$. After 8 h, a green

formed solid, suitable for X-ray analysis, had crystallized. Drying under vacuum afforded 124 mg of **11** (77% yield). Elemental analysis (%) calcd for $C_{50}H_{46}Cl_6P_2PtTi_2$: C, 49.53; H, 3.82. Found: C, 51.47; H, 4.72 (the values may be attributed to partial loss of dichloromethane from the crystalline sample). 1H NMR (600 MHz, dichloromethane- d_2): δ 7.80–7.03 (m, 10H, $P(C_6H_5)_4$), 5.70 (s, 7H, C_7H_7), 5.60 (m, 2H, C_5H_4), 5.46 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (150.9 MHz, dichloromethane- d_2): δ 134.4 (m, *i*- C_6H_5), 131.2 (m, *o*- C_6H_5), 128.5 (m, *p*- C_6H_5), 125.5 (m, *m*- C_6H_5), 105.6 (m, *i*- C_5H_4), 103.3 (m, α - C_5H_4), 100.4 (m, β - C_5H_4), 88.3 (s, C_7H_7). $^{31}P\{^1H\}$ NMR (161.9 MHz, dichloromethane- d_2): δ 6.7 (s, PPh_2C_5 , $^1J_{Pt-P} = 2634$ Hz).

X-ray Crystal Structure Determinations. Data were recorded on area detectors (Oxford Diffraction) at low temperature. Absorption corrections were performed on the basis of multiscans. Structures were refined anisotropically using the program SHELXL-97.⁵² Hydrogen atoms were included using rigid methyl groups or

a riding model. Numerical details are summarized in Table 1. Special features and exceptions: for compounds **4–6**, **8** and **11**, H atoms of the rings were refined freely but with C–H distances constrained equally. For compounds **5**, **7**, and **9**, which crystallize by chance in noncentrosymmetric space groups, the Flack parameter refined to 0.379(5) (racemic twin), 0.016(15), and 0.005(5), respectively. The two dichloromethane molecules of structure **10** are both disordered (one over an inversion center). The crystal of compound **7** was twinned, but the closeness of β to 90° prevented successful untwinning despite repeated efforts. For this reason, the *R* values and residual electron density are unsatisfactory.

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Supporting Information Available: CIF files for each of the crystal structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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