During the course of refereeing of this manuscript, a report of the reaction of triplet fluorenylidene with olefins demonstrated that "negative activation energies" also occur in some of these systems. The effect was attributed to reversible formation of *triplet* carbene–alkene complexes that are precursors to the final products.[14]

Acknowledgment. We thank the National Science Foundation for its generous support of this work. We also thank Dr. I. R. Gould for his assistance in extending the initial data points employed to generate Figures 1 and 2 and Dr. J. C. Scaiano for an independent determination of k_{abs} for the reaction of PhCCl and **1**. The authors thank Professor Cheves Walling for his thoughtful comments and suggestions.

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Synthesis and Structural Investigation of (Mesityl(diphenylmethylene)phosphine)bis(triphenylphosphine)platinum(0)

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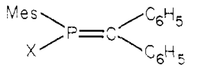
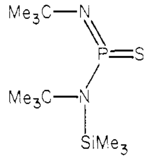
Mesityl(diphenylmethylene)phosphine (**1**)[1] is one of the few



1, X = lone pair
2, X = Cr(CO)$_5$
Mes = mesityl

known thermally stable phosphaalkenes with an essentially localized P=C double bond. The chemistry of this new class of compounds is just beginning to be developed.[2] It has been shown that **1** can act as an η^1 (σ P or "end-on") ligand toward metal centers,[3,4] as illustrated by the pentacarbonylchromium(0) complex **2**.[3]

It was of interest to investigate if the P=C function was also suited for η^2 (π or "side-on") coordination. For this purpose, Pt(0) is particularly favorable as it is known to undergo η^2 coordination not only with C=C bonds but also with a great variety of heteroalkenes, e.g., with the C=S bond of CS$_2$[5] or of sulfines,[6] the N=S bond of sulfinylanilines,[7] the P=S bond of the metathiophosphoric acid derivative **3**,[8] and even the P=P bond of the phosphorobenzene derivative **4**.[9]



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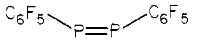

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Table I. ^{31}P NMR Spectrum (101.26 MHz) of 5

	δ^a	$^1J_{PtP}{}^b$	$^2J_{PP}{}^b$
P1	21.94	3359	P1P2, 29.6
P2	22.23	3392	P2P3, 11.1
P3	−33.48	505	P3P1, 56.4

^{a} In ppm relative to external 85% H$_3$PO$_4$; toluene-d_{18}; −56.5 °C. ^{b} In Hertz.

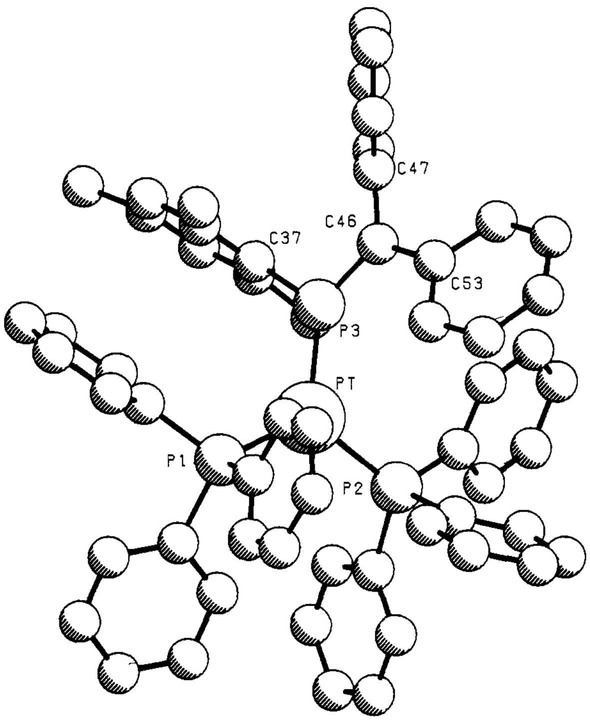

Figure 1. Structure of (mesityl(diphenylmethylene)phosphine)bis(triphenylphosphine)platinum(0).

We now report the synthesis of (PPh$_3$)$_2$Pt(MesP=CPh$_2$) (**5**). According to its NMR spectra and its X-ray crystal structure determination, **5** presents an unusual Pt–P bonding situation.

Dark red crystals of **5** (mp 194–199 °C) were obtained in almost quantitative yield from the 1:1 reaction of (PPh$_3$)$_2$Pt(C$_2$H$_4$) (**6**) with **1** in toluene at room temperature. Elemental analyses confirmed the proposed stoichiometry. A field desorption mass spectrum[10] indicated a monomeric structure. At room temperature, the ^{1}H and ^{31}P NMR spectra were broad; however, at −55 ± 1 °C, the ^{31}P NMR spectrum was sharp and showed interesting features (Table I). While the ^{31}P parameters of the two *nonequivalent* triphenylphosphine ligands are normal, those of ligand **1** are quite unusual: the δ value (−33.5) is shifted 266.5 ppm toward higher field from that of free **1**^{1} (compare the relatively small shifts in η^1-bonded compounds[3,4] such as **2** (4.2 ppm

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(10) Field desorption mass spectrum: m/z 1034 $(C_{58}H_{51}P_3{}^{194}Pt)^{+\cdot}$; isotope pattern as expected for Pt; no fragmentation.

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downfield relative to **1**)); $^1J_{PtP}$ has the surprisingly low value of 505 Hz. We felt that (a) the nonequivalence of P1 and P2, (b) the upfield shift of the resonance of P3 (cf. the similar, though less dramatic trend, for **3**[8]), and (c) the weak PtP3 coupling strongly indicated η^2-coordination for **5** in solution.

So that this conclusion could be checked, an X-ray crystal structure determination of **5** was carried out.[11] The structure (Figure 1) shows discrete monomeric units in which the Pt atom has a distorted trigonal coordination. All three P atoms are in one plane with Pt and are σ coordinated to the metal. The Pt-P1 and Pt-P2 bond lengths are in the usual range (228.8 (3) and 229.4 (3) pm, respectively); the Pt-P3 bond is shorter (221.8 pm), as expected for a sp^2 hybridized P atom.[3] Interestingly, the least-squares planes through PtP1P2P3 and PtP3C37C46 form an angle of 67.4° (Figure 2, supplementary material). The near-planarity of PtP3C46C47C53 and the Pt–C46 distance (357 (1) pm) exclude any η^2-type interaction. As in **2**,[3] the ligand **1** is hardly affected structurally by coordination to Pt(0). A noteworthy feature of **1** in **5** is the P=C bond length of 165 (1) pm, which is even shorter than that of CH_2=PH (167.0 pm[12]); there appears to be a trend of P=C bond shortening from **1** (170 pm[2,13]) via **2** (167.9 (4) pm[3]) to **5**. The bond angle at phosphorus (C37–P3–C46, 108.5 (5)°) is smaller than 120° (the angle expected for ideal sp^2 hybridization) but similar to that in free **1** (108.7°) and in **2** (109.8 (2)°).

We are thus left with the somewhat puzzling situation that the ^{31}P NMR and the X-ray data seem to be at variance. Two possible explanations might resolve this apparent discrepancy. First, one might assume that in **5**, **1** is η^1-coordinated and acts as an unusually weak σ donor (as reflected by the small $^1J_{PtP3}$) and an unusually strong π acceptor[14] (as reflected by the strong upfield shift of δ P3). However, at present it is not clear why **1** should behave so differently in **5** and in **2**, where it has been identified as a σ donor and a π acceptor of intermediate strength;[3] moreover, strong π back-donation should result in lengthening of the P=C bond,[14] while the reverse is observed.

A second plausible possibility would be the occurrence of two different structures of **5** in solution and in the crystalline state. In the crystal, η^1-coordination is unambiguously established by the X-ray data. In solution, the bonding situation may have changed to η^2-coordination; the dynamic effects observed in the NMR spectra above −50 °C may be an indication of rapid transformations of this kind. A coordinatively saturated P atom in solution is indicated by the observation that **5** did not react with a second equivalent of **1** or with triphenylphosphine; this behavior is more in line with an η^2 coordination than with an η^1 coordination. On the other hand, in the η^2-coordination mode, **1** would not make use of its HOMO, which is a σ orbital essentially located as a lone pair on phosphorus.[14]

Clearly, further investigations are required before a decision between these interesting alternatives can be made; these investigations are in progress.

Acknowledgment. We thank R. Fokkens, University of Amsterdam, for measuring the field desorption mass spectra.

Registry No. 5, 80737-43-5; **6**, 12120-15-9.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond lengths, and bond angles and Figure 2 (7 pages). Ordering information is given ony any current masthead page.

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(11) The crystals of **5** were triclinic and crystallized in space group $P\bar{1}$, $Z = 2$, with unit cell constants a = 12.286 (2) Å, b = 13.948 (2) Å, c = 14.875 (3) Å, α = 100.99 (2)°, β = 94.88 (2)°, γ = 101.43 (2)°. A total of 6698 reflexions with intensity above the 2.5σ level were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Mo Kα radiation. No absorption correction was applied. The structure was derived directly from an E^2-Patterson synthesis. Refinement proceeded by anisotropic block-diagonal least-squares calculations. Most of the H atoms were indicated in a difference Fourier synthesis and were introduced and kept fixed at their calculated positions. The final R value was 0.062. A final difference Fourier synthesis showed effects of absorption around Pt and also a large number of peaks of heights of about 0.8 e/Å^3, which could not be interpreted but which are undoubtedly due to some form of disorder. Relevant bond distances (in pm): Pt–P1, 228.8 (3); Pt–P2, 229.4 (3); Pt–P3, 221.8 (3); P3–C46, 165 (1); P3–C37, 182 (1); C46–C47, 156 (2); C46–C53, 151 (2); P1–C1, 187 (1); P1–C7, 183 (1); P1–C13, 185 (1); P2–C19, 182 (1); P2–C25, 182 (1); P2–C31, 180 (1). Relevant bond angles (in degrees): P1–Pt–P3, 120.6 (1); P2–Pt–P1, 121.9 (1); P2–Pt–P3, 117.3 (1); Pt–P3–C46, 133.3 (5); Pt–P3–C37, 118.2 (3); C46–P3–C37, 108.5 (5); C53–C46–P3, 122.6 (8); C53–C46–C47, 133.3 (8); C47–C46–P3, 124.0 (8).

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Interaction of Ions with the Surface Receptor of the Azobenzene-Containing Bilayer Membrane. Discrimination, Transduction, and Amplification of Chemical Signals

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We describe in this article how unique properties of the bilayer membrane are advantageously used for preparing molecular systems in which discrimination, transduction, and amplification of chemical signals are possible.

It has been shown that the bilayer membrane is formed from a variety of single-chain and double-chain amphiphiles which are not directly related to the structure of biolipids.[1] The fundamental physicochemical characteristics of the synthetic bilayer membrane are the same as those of the biolipid bilayer, and therefore, it is expected that some of the molecular machinery of the cell membrane[2] is reproducible by using the synthetic system.

As reported before,[3,4] ammonium amphiphiles with the azobenzene chromophore form stable bilayer assemblies in water. The absorption maximum of this chromophore may undergo hypsochromic shifts in the bilayer matrix relative to that in homogeneous solutions. This spectral shift was used to detect phase separation in the dialkylammonium membrane matrix.[5] The phase-separation phenomenon is useful for the present purpose. The membrane-forming amphiphiles used in the present study are given in Chart I.[6]

In a mixed bilayer membrane of **1** and **4** (molar ratio, 1:10), amphiphile **1** exists as an isolated species at temperatures above T_c (28 °C) of the matrix membrane of **4**. The absorption maximum of the azobenzene chromophore is located at 355 nm in this case, in agreement with that in ethanol. From a drop in temperature, λ_{max} shifts to 320 nm, indicating formation of the clustered species of **1**.

The phase separation depends on the molecular structure of the azobenzene amphiphile. Thus, amphiphile **2**, which possesses a shorter alkyl tail, does not undergo phase separation under the

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