Influence of Steric Factors on the Coordination Mode (η^1 or η^2) of Phosphaalkenes to Zerovalent Pt^0L_2 Centers. X-ray Structure of Bis(triphenylphosphine){(2,6-dimethylphenyl)-9-fluorenylidenephosphine}platinum(0)–Toluene

Johanna G. Kraaijkamp and Gerard van Koten*

Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands

Theo A. van der Knaap and Friedrich Bickelhaupt

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Casper H. Stam

Laboratorium voor Kristallografie, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam,
The Netherlands

Received October 24, 1985

New phosphaalkene–platinum(0) complexes, $Pt(PCy_3)_2(XylP{=}CPh_2)$ (**4**) (Xyl = 2,6-dimethylphenyl) and $Pt(PPh_3)_2(C_{12}H_8C{=}PXyl)$ (**6**), have been prepared by reacting the respective phosphaalkenes with the corresponding "$Pt(PCy_3)_2$" and "$Pt(PPh_3)_2$" precursors. ^1H and ^{31}P NMR spectra showed that the phosphaalkene ligand is η^1-P-coordinated in **4** ($\delta(^{31}P_{\text{free ligand}}) - \delta(^{31}P_{\text{complex}} = \Delta\delta(^{31}P) = 12.7$ ppm; $^1J(^{31}P,^{195}Pt) = 4475$ Hz) but η^2-P=C-bonded in **6** ($\Delta\delta(^{31}P) = 277$ ppm; $^1J(^{31}P,^{195}Pt) = 319$ Hz). ^{31}P NMR spectra of **4** and **6** at different temperatures (range −60 to +40 °C) revealed that the $\eta^1\text{-P} \rightleftarrows \eta^2\text{-P=C}$ equilibrium established for the phosphaalkene bonding mode in $Pt(PPh_3)_2(MesP{=}CPh_2)$ (**1**) (Mes = mesityl) does not exist in the case of **4** and **6**; the latter complexes are examples of the extreme situations in this equilibrium, i.e., either η^1-P (**4**) or η^2-P=C (**6**) coordination. The structure of **6** has also been studied by X-ray diffraction (see Figure 1): monoclinic, space group $P2_1/n$, $Z = 4$ with cell constants $a = 13.228$ (2) Å, $b = 17.086$ (1) Å, $c = 23.353$ (2) Å, $\beta = 102.92$ (1)°, $V = 5144.5$ (7) Å^3, $d_{\text{calcd}} = 1.45$ g cm^{-3}, and μ(Cu Kα) = 63.5 cm^{-1}. The structure was refined to a final R of 0.031 for 6113 observed reflections above the $2.5\sigma(I)$ level. Characteristic structural features of **6** are the η^2-P=C bonding mode of the phosphaalkene with an elongated P=C bond of 1.814 (4) Å, as well as the small value of the P(1)–Pt–P(2) angle of 98.92 (5)°. The Pt–P distances are 2.302 (1) and 2.318 (1) Å with the PPh_3 ligands and 2.356 (1) Å with the phosphaalkene. On the basis of the nature of the frontier orbitals involved when combining the ML_2 and the P=C fragments in **4** and **6**, respectively, the specific coordination mode encountered in these complexes is discussed. It appears that the actual coordination mode is connected to the interligand bond angles that can be realized in a L–M–L fragment. For steric reasons the PCy_3–Pt–PCy_3 angle in **4** will be large ($\simeq$170°) which makes the σ-donation component in the PtL_2—P=C bonding more important and hence stabilizes the η^1-P bonding mode. In contrast, the PPh_3–Pt–PPh_3 angle can be as small as about 99°; in this situation extensive electron transfer from the Pt d_{xz} into the π^* P=C can take place which stabilizes the η^2-P=C bonding as found in **6**.

Introduction

Recent studies have shown that the intrinsically unstable phosphaalkenes[1] can be stabilized by coordination to metal centers.[2] Computational studies[1b,3] showed that the phosphorus lone-pair σ-orbital and the π-orbital of the P=C bond are of nearly equal energy with the σ-orbital most likely to be the HOMO.[1b] This result is in line with the recently reported crystal structures of complexes in which the phosphaalkene ligand $R^1P{=}CR_2$ is either η^1-P-bonded, e.g., to $Cr(CO)_5$,[2a] *trans*-$PtCl_2(PPh_3)$,[2b] or $Pt(PPh_3)_2$ (see **1a** in eq 1),[2c] or η^2-P=C-bonded, e.g., to Pt(triphos),[2d] Ni(bpy),[2e] or $Ni(PMe_3)_2$.[2f]

Except for **1a** the respective coordination modes found in the solid are retained in solution. In the case of $Pt(PPh_3)_2(MesP{=}CPh_2)$ (**1**), ^{31}P and ^{195}Pt NMR spectrometry revealed that, whereas in the solid state $MesP{=}CPh_2$ (**2**) is coordinated in the η^1-mode (**1a**; confirmed by X-ray[2c] and solid-state ^{31}P NMR[2c,g]), in solution the equilibrium **1a** $\rightleftharpoons$ **1b** shown in eq 1 exists. Experimental evidence pointed to a slightly better stability of the η^2-bonding mode in **1b**. This is to our knowledge the first example of a directly observable equilibrium between the two coordination modes for a phosphaalkene. A theoretical analysis by Hartree–Fock–Slater (LCAO-Xα) calculations[2c] on the

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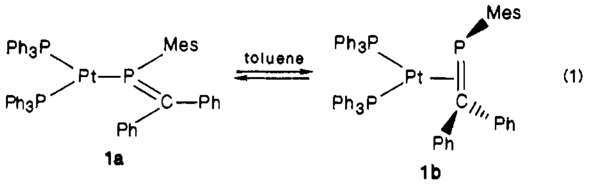


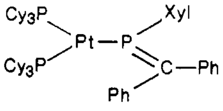
1a 1b

ΔH = • 4 kcal/mol
ΔS = -15 kcal/(mol deg)

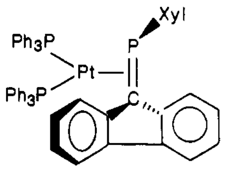
model system $Pt(PH_3)_2(HP{=}CH_2)$ confirmed that the η^2-mode is energetically slightly favored over η^1-bonding due to the stronger back donation from a metal d_{xz} orbital into the low-lying[1b] π^* orbital. However, it was also obvious that the differences are small and most likely can be cancelled or even overruled by a change in the bulkiness or electronic properties (π-donating vs. π-accepting) of the coligands.

That indeed the coordination mode of the phosphaalkene can be steered to either η^1- or η^2-bonding by changing the electronic properties of the coligands has recently been shown by substitution of the weakly π-accepting bpy ligand in $Ni(bpy)(\eta^2\text{-}XylP{=}CPh_2)$ by the strongly π-accepting CO ligands in $Ni(CO)_3(\eta^1\text{-}XylP{=}CPh_2)$.[2e]

In this paper we report on the influence of steric factors, on the side either of the L_2Pt fragment or of the phosphaalkene, on the actual coordination mode of the phosphaalkene. When $Pt(PPh_3)_2$ in **1** is replaced by the sterically much more demanding $Pt(PCy_3)_2$ group, the exclusive occurrence of η^1-coordination of the phosphaalkene $XylP{=}CPh_2$ (**3**) is observed in **4** (Xyl = 2,6-dimethylphenyl).



4



6

On the contrary, a complete change from the η^1- to the η^2-coordination mode has been achieved by coordinating $Pt(PPh_3)_2$ to (2,6-dimethylphenyl)-9-fluorenylidenephosphine (**5**).[4] In this phosphaalkene ligand the two C-aryl rings are forced into one plane with the P=C bond. This makes the P=C bond in **5** much more accessible for π-coordination than that in **2** or **3**. The opposite applies for the accessibility of the σ lone pair which in the case of **5** is hindered by the aromatic proton at C(1) of the fluorene moiety. An X-ray structure determination and ^1H, ^{195}Pt, and ^{31}P NMR studies revealed that **5** is exclusively coordinated in the η^2-P=C coordination mode to $Pt(PPh_3)_2$ in complex **6** both in the solid state and in solution.

Experimental Section

All preparations were carried out under oxygen-free dry nitrogen. The solvents were carefully dried and distilled before use. The complexes $[Pt(PPh_3)_2C_2H_4]$ and $[Pt(COD)_2]$ and the phosphaalkene ligands[1b,4] were prepared by published methods. The ^1H, ^{31}P and ^{195}Pt NMR spectra were recorded on a Bruker WM 250 spectrometer. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Applied Chemistry TNO (Zeist, The Netherlands).

Bis(tricyclohexylphosphine){(2,6-dimethylphenyl)(diphenylmethylene)phosphine}platinum(0), $[Pt(PCy_3)_2(\mathbf{3})]$ (**4**).

To a suspension of $[Pt(COD)_2]$ (0.37 mmol, 150 mg) in 4 mL of pentane was added PCy_3 (0.72 mmol, 200 mg) in 2 mL of toluene in about 5 min. To the resulting yellowish solution was added the phosphaalkene **3** (0.36 mmol, 110 mg) in 1 mL of toluene in 2 min. The dark red solution was stirred for 30 min and evaporated to dryness. This product was used for spectroscopic investigation without further purification.

Bis(triphenylphosphine){(2,6-dimethylphenyl)-9-fluorenylidenephosphine}platinum(0), $[Pt(PPh_3)_2(\mathbf{5})]$ (**6**).

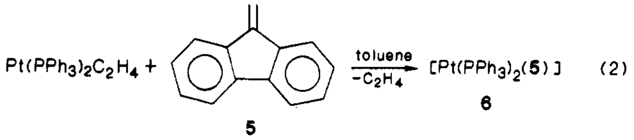
A solution of **5** (0.14 mmol, 42 mg) in 0.7 mL of toluene was added to $[Pt(PPh_3)_2C_2H_4]$ (0.14 mmol, 106 mg) in 0.5 mL of toluene. The resulting red-violet solution was connected to a tube with pentane; as a result of vapor diffusion of the pentane into the toluene solution, after about 15 h, yellow crystals were precipitated. The solution was removed; the crystals were washed with pentane and dried in vacuo; yield 80%. Recrystallization from warm toluene yielded crystals of the toluene solvate $[Pt(PPh_3)_2(\mathbf{5})]\cdot C_7H_8$. Anal. Calcd for $C_{64}H_{55}P_3Pt$: C, 69.12; H, 4.98; P, 8.36. Found: C, 68.36; H, 5.29; P, 7.90. FD/MS: m/z 1020 ($\mathbf{6}^{\bullet+}$).

X-ray Structure Determination of $C_{57}H_{47}P_3Pt{\cdot}C_7H_8$ (6). Crystals of the title compound are monoclinic of space group $P2_1/n$ with $Z = 4$. The cell constants, derived from 23 reflections, with $75.9 < 2\theta < 79.5°$, are $a = 13.228$ (2) Å, $b = 17.086$ (1) Å, $c = 23.353$ (2) Å, $\beta = 102.92$ (1)°, $V = 5144.5$ (7) Å^3, $d_{calcd} = 1.45$ g cm^{-3}, and μ(Cu Kα) = 63.5 cm^{-1}. Crystal dimensions: 0.06 × 0.11 × 0.21 mm. A total of 9096 intensities were measured on a Nonius CAD4 diffractometer using graphite-monochromated Cu Kα radiation. A total of 2956 reflections were below the $2.5\sigma(I)$ level and were treated as unobserved.

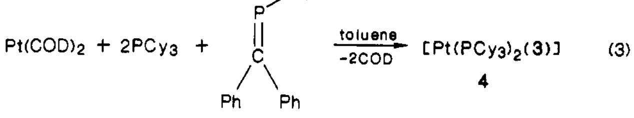
The structure was solved by means of the heavy-atom technique and refined by means of block-diagonal least-squares calculations. A ΔF Fourier revealed the presence of one molecule of toluene. Since its electron density was not very well-defined, a toluene molecule of ideal geometry was introduced and refined as a rigid body with one overall isotropic temperature parameter ($U = 0.24$ Å^2). An empirical absorption correction[5] was applied. The ring hydrogen atoms, which were indicated in a ΔF Fourier were introduced at their calculated positions ($U = 0.06$ Å^2) and not refined. A weighting scheme, $w = 1/(4.1 + F_o + 0.025F_o^2)$, was employed, and the anomalous dispersion of Pt and P was taken into account. The final R value for the 6113 observed reflections was 0.031 ($R_w = 0.047$). The atomic coordinates of Pt, P, and C atoms are given in Table I. The calculations were performed with X-Ray 76.[6a] The scattering factors were taken from Cromer and Mann;[6b] the dispersion corrections from ref 6c.

Results

Syntheses of the Complexes. The phosphaalkene complexes **4** and **6** have been prepared via the routes shown in eq 2 and 3. The novel complex **6** is a yellow crystalline solid which dissolves in toluene to give red-violet solutions [λ_{max} 520 nm (ϵ 3443)]. The $Pt(PCy_3)_2(XylP{=}$



5 **6**



3 **4**

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[5] Walker, N.; Suart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

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Table I. Atomic Coordinates Pt, P, and C Atoms of $C_{57}H_{47}P_3Pt \bullet C_7H_8$ (6)[a,b]

atom	x	y	z
Pt1	0.22890 (1)	0.19479 (1)	0.10239 (1)
P1	0.3352 (1)	0.10949 (7)	0.06577 (5)
P2	0.1688 (1)	0.26831 (7)	0.01915 (5)
P3	0.1817 (1)	0.24571 (8)	0.18647 (6)
C1	0.4387 (4)	0.1635 (3)	0.0425 (2)
C2	0.4778 (4)	0.1482 (3)	−0.0070 (3)
C3	0.5606 (6)	0.1904 (4)	−0.0173 (4)
C4	0.6052 (5)	0.2489 (5)	0.0202 (4)
C5	0.5676 (5)	0.2656 (4)	0.0691 (4)
C6	0.4834 (5)	0.2229 (4)	0.0803 (3)
C7	0.2658 (4)	0.0484 (3)	0.0056 (2)
C8	0.1574 (4)	0.0501 (3)	−0.0064 (2)
C9	0.1002 (4)	0.0061 (3)	−0.0522 (2)
C10	0.1485 (5)	−0.0402 (4)	−0.0855 (3)
C11	0.2550 (4)	−0.0463 (3)	−0.0727 (3)
C12	0.3135 (4)	−0.0017 (3)	−0.0269 (3)
C13	0.4103 (4)	0.0339 (3)	0.1133 (2)
C14	0.3614 (5)	−0.0345 (3)	0.1234 (3)
C15	0.4189 (7)	−0.0925 (4)	0.1607 (3)
C16	0.5204 (6)	−0.0824 (5)	0.1852 (3)
C17	0.5689 (5)	−0.0138 (5)	0.1761 (3)
C18	0.5150 (5)	0.0466 (4)	0.1411 (3)
C19	0.0361 (4)	0.2466 (3)	−0.0197 (2)
C20	−0.0278 (4)	0.2026 (3)	0.0078 (3)
C21	−0.1307 (5)	0.1877 (4)	−0.0222 (4)
C22	−0.1691 (5)	0.2148 (4)	−0.0769 (3)
C23	−0.1063 (5)	0.2567 (4)	−0.1049 (3)
C24	−0.0049 (5)	0.2723 (4)	−0.0776 (3)
C25	0.2377 (4)	0.2638 (3)	−0.0411 (2)
C26	0.2118 (5)	0.2043 (4)	−0.0842 (3)
C27	0.2701 (7)	0.2003 (4)	−0.1278 (3)
C28	0.3480 (7)	0.2540 (5)	−0.1304 (4)
C29	0.3691 (7)	0.3091 (4)	−0.0900 (5)
C30	0.3153 (6)	0.3153 (4)	−0.0441 (3)
C31	0.1716 (4)	0.3743 (3)	0.0331 (3)
C32	0.2195 (7)	0.4044 (4)	0.0867 (3)
C33	0.2235 (8)	0.4829 (5)	0.0965 (4)
C34	0.1805 (7)	0.5357 (4)	0.0546 (4)
C35	0.1290 (8)	0.5072 (5)	0.0027 (5)
C36	0.1257 (7)	0.4279 (4)	−0.0094 (4)
C37	0.2537 (4)	0.1547 (3)	0.1913 (2)
C38	0.2159 (4)	0.0745 (3)	0.1977 (2)
C39	0.1234 (4)	0.0386 (3)	0.1702 (3)
C40	0.1066 (5)	−0.0398 (4)	0.1826 (3)
C41	0.1812 (6)	−0.0804 (4)	0.2238 (3)
C42	0.2734 (5)	−0.0452 (4)	0.2513 (3)
C43	0.2914 (4)	0.0318 (3)	0.2380 (2)
C44	0.3823 (4)	0.0810 (3)	0.2556 (2)
C45	0.4806 (5)	0.0662 (4)	0.2937 (2)
C46	0.5559 (5)	0.1245 (5)	0.3000 (3)
C47	0.5364 (5)	0.1967 (4)	0.2715 (3)
C48	0.4389 (5)	0.2122 (3)	0.2358 (3)
C49	0.3622 (4)	0.1545 (3)	0.2273 (2)
C50	0.0493 (4)	0.2229 (3)	0.1953 (2)
C51	−0.0369 (4)	0.2600 (3)	0.1586 (2)
C52	−0.1382 (5)	0.2437 (5)	0.1639 (3)
C53	−0.1537 (6)	0.1899 (4)	0.2053 (4)
C54	−0.0682 (6)	0.1597 (4)	0.2474 (3)
C55	0.0321 (5)	0.1773 (3)	0.2436 (3)
C56	−0.0235 (5)	0.3251 (4)	0.1170 (3)
C57	0.1195 (6)	0.1519 (5)	0.2938 (3)
C58	0.6147	0.4148	0.2576
C59	0.6176	0.4375	0.1957
C60	0.5255	0.4533	0.1550
C61	0.5282	0.4743	0.0976
C62	0.6230	0.4796	0.0811
C63	0.7151	0.4639	0.1219
C64	0.7124	0.4429	0.1793

[a] Atomic coordinates of the hydrogen atoms are available as supplementary material (Table A). [b] Estimated standard deviations in parentheses.

CPh_2) complex **4** had to be prepared starting from Pt($COD)_2$ which was converted in situ into "$Pt(PCy_3)_2$" and subsequently reacted with **3** (eq 3). The resulting complex **4** is extremely soluble in toluene and pentane to give dark red solutions [λ_{max} 440 nm (ϵ 7123)].

The pure compounds whose stoichiometry had been established by elemental analysis (see Experimental Section for **6**) and by ^{31}P (see Table II) and ^1H NMR spectrometry are stable in solution but only in an inert atmosphere.

The bonding of the phosphaalkene ligand to the bis(phosphine)platinum unit can be inferred from the ^{31}P NMR data of the complexes (see Table II). The NMR data for **6** have been obtained at −52 °C. Observations that establish the η^2-coordination mode for the phosphaalkene **5** (which is also present in the solid, vide infra) are the very large upfield shift of P(3) by approximately 277 ppm (as compared with that of free **5**)[4] as well as the extremely small $^1J(^{195}Pt,^{31}P(3))$ of 319 Hz. These data are similar to those of $Pt(PPh_3)_2(\eta^2\text{-MesP}{=}CPh_2)$ (isomer **1b**) for which η^2-P=C bonding was derived from the ^{31}P NMR data.[2c] The ^{195}Pt NMR spectrum of **6** (see Table III) shows exclusively a resonance at −4847 ppm which can now be considered as a typical value for η^2-bonding of phosphaalkenes.

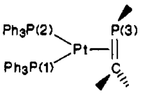
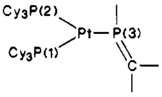
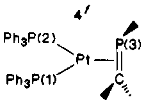
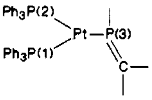
The occurrence of an $\eta^2 \rightleftarrows \eta^1$ equilibrium (cf. eq 1) in the case of **6** could be excluded because even at room temperature no signal indicative for η^1-coordination (cf. data for **1a**)[2c] was observed. At temperatures above +50 °C, the ^{195}Pt multiplet disappeared completely without coalescence while on subsequent cooling to −55 °C the initial spectrum was again observed. It must be noted that also the ^{31}P NMR spectrum starts to broaden at temperatures above −50 °C probably as a result of dynamic effects (cf. the similar temperature behavior of **1**).[2c]

The assignments of P(1) as trans to P(3) and accordingly P(2) as cis to P(3) are based on the values of the $^2J(^{31}PPt^{31}P)$ which are 62 and 7 Hz, respectively. As pointed out in a previous paper for the assignment of the ^{31}P chemical shifts in **1a** and **1b**, this is based on the fact that in planar arrangements cis couplings are generally smaller than trans couplings. Whereas in **1b** the J_{trans} to J_{cis} ratio was only about 3, for the present compound this ratio is found to amount to almost 9.[2h]

The $Pt(PCy_3)_2(XylP{=}CPh_2)$ complex **4** contains an η^1-bonded phosphaalkene as indicated by the ^{31}P NMR parameters at room temperature (see Table II). Especially the only small upfield shift of P(3) ($\Delta\delta$ = 12.7 ppm) which is comparable to that observed for P(3) in **1a** indicates a similarity in structure. The equivalence of P(1) and P(2) indicates that a dynamic process occurs which creates an apparent molecular symmetry plane containing the phosphaalkene skeleton and bisecting the PPtP angle. This process could involve either fast rotation around the P(3)–Pt bond or, more likely, an oscillation between skew positions (cf. solid-state structure of $Pt(PPh_3)_2(\eta^1\text{-MesP}{=}CPh_2)$ (**1**), which shows an angle of 67° between the P—Pt—P and Pt—P=C planes).

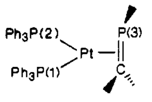
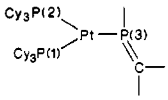
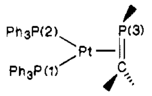
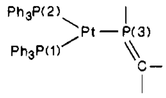
Comparison of the $^1J(^{195}Pt,^{31}P)$ data of **1a** and **4** reveals a smaller $^1J(^{195}Pt,^{31}P(3))$ value in **4** than in **1a**. This may be caused by the higher basicity of the PCy_3 ligand as compared with PPh_3. Accordingly, the P_2Pt fragment in **4** will have a lower σ-acceptor capacity, which then would result in a lower s-electron density in the Pt–P(3) bond and thus give rise to a smaller $^1J(^{195}Pt,^{31}P(3))$ value. In the ^{31}P and ^{195}Pt NMR spectra no trace of the η^2-bonded compound could be observed. This indicates that when the nature of the phosphine in the bis(phosphine)platinum unit is changed, the balance between η^1- and η^2-bonding of the phosphaalkene is shifted in favor of the η^1-bonding mode.

Table II. ^{31}P NMR Data of the Bis(triorganophosphine) Phosphaalkene Complexes 1a, 1b, 4, and 6

compd[a]	$\delta(^{31}P)$			$^1J(^{195}Pt,^{31}P)$, Hz			$^2J(^{31}P,^{31}P)$, Hz		
	P(1)	P(2)	P(3)[b]	P(1)	P(2)	P(3)	P(1,2)	P(1,3)	P(2,3)
 6[c]	25.2	26.2	−34.7 (242.5)[d]	3754	3089	319	15	62	7
 4[f]	61.1	61.1	245.2 (232.5)[e]	4335	4335	4475	0	151	151
 1b[g]	22.4	25.0	−30.3 (233.0)[e]	3403	3367	500	31	56	10
 1a[g]	48.0	48.0	247.5 (233.0)[e]	4354	4354	4964	0	156	156

[a] Structure shown according to assignment $\delta(^{31}P)$ in parts per million relative to external 85% H_3PO_4. [b] $\delta(^{31}P)$ of the free phosphaalkene in parentheses. [c] At −52 °C, in toluene-d_8; 102.25 MHz. [d] See ref 4. [e] See ref 1b. [f] At ambient temperature, in toluene-d_8; 102.25 MHz. [g] At −70 °C; 102.25 MHz.

Table III. ^{195}Pt NMR Data of the Bis(triorganophosphine) Phosphaalkene Complexes 1a, 1b, 4, and 6

compd[a]	$\delta(^{195}Pt)$[b]	$^1J(^{195}Pt,^{31}P)$, Hz			T, °C
		PtP(1)	PtP(2)	PtP(3)	
 6	−4885	3762	3093	320	−55
 4	−4273	4341	4341	4475	RT
 1b[c]	−4847	3380[d]	3380[d]	500	−40
 1a	−4410	4360	4360	4940	−40

[a] Schematic structure shown according to assignment. [b] Relative to external K_2PtCl_6 (0.5 M in D_2O) in ppm: in toluene-d_8. [c] See ref 1c. [d] Not resolved.

In order to establish unambiguously the η^2-P=C coordination in 6 already anticipated from ^{31}P and ^{195}Pt NMR data, we carried out an X-ray structure determination of 6.

Molecular Geometry of $Pt(PPh_3)_2(C_{12}H_8C{=}PC_6H_3Me_2\text{-}o,o')\cdot C_6H_5CH_3$. The structure of 6 in the crystalline state consists of four molecules per unit cell. The molecular geometry and the adopted numbering scheme are shown in Figure 1. All bond lengths and angles (see Table IV) are within the expected ranges.

The coordination around platinum is approximately planar and comprises the phosphine atoms of the two PPh_3 ligands as well as the phosphaalkene fragment P(3)–C(37). Deviations from the least-squares planes through Pt, P(3), and C(37) are only 0.39 and −0.09 Å, for the respective phosphorus atoms of the two PPh_3 ligands.

The observed geometries around P(3) and C(37) are characteristic for atoms of a heteroolefinic bond that is involved in η^2-coordination to a metal center. The plane of the fluorene unit is almost perpendicular (84°) to the plane through C(37), P(3), and Pt. The angle of 30.9° between the P(3)–C(37) axis and the least-squares plane through the fluorene skeleton is a clear indication for a change in hybridization of C(37) from sp^2 in the free ligand 5 toward sp^3 in the coordinated ligand in 6. This geometrical change is similar to that observed for the heteroolefinic substituents in $K[PtCl_3(C_2H_4)]$ (16°),[7a] $Pt(PPh_3)_2(C_{12}H_8C{=}S{=}O)$ (7, 32°),[7b] and $Pt(PPh_3)_2(2,4,6\text{-}Me_3C_6H_2N{=}S{=}O)$.[7c] The P(3)–C(Xyl) bond is also bent out of the original $C_{12}H_8C{=}P(3)$ plane. The actual dihedral angle between the plane which includes P(3) and C(37) and is perpendicular to C(37), P(3), Pt and the plane C(37), P(3), C(50) amounts to 20.9°, whereas 0° would be expected in the absence of η^2-P=C coordination.

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[7] (a) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653. (b) Gosselink, J. W.; van Koten, G.; Spek, A. L.; Duisenberg, A. J. M. *Inorg. Chem.* **1981**, *20*, 877. (c) Meij, R.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1979**, *164*, 353 and references cited therein.

Table IV. Bond Distances (Å) and Bond Angles (deg) of 6[a]

Bond Distances

Pt1–C37	2.141 (3)	C13–C14	1.381 (6)	C27–C28	1.392 (9)	C42–C43	1.385 (6)
Pt1–P1	2.3175 (9)	C13–C18	1.408 (6)	C28–C29	1.317 (9)	C43–C44	1.450 (6)
Pt1–P2	2.3017 (8)	C13–P1	1.842 (4)	C29–C30	1.417 (9)	C44–C45	1.426 (6)
Pt1–P3	2.5557 (10)	C14–C15	1.422 (7)	C31–C32	1.370 (7)	C44–C49	1.415 (5)
C1–C2	1.391 (6)	C15–C16	1.349 (8)	C31–C36	1.386 (7)	C45–C46	1.393 (7)
C1–C6	1.387 (6)	C16–C17	1.375 (8)	C31–P2	1.839 (4)	C46–C47	1.398 (7)
C1–P1	1.832 (4)	C17–C18	1.407 (7)	C32–C33	1.360 (8)	C47–C48	1.396 (7)
C2–C3	1.376 (7)	C19–C20	1.391 (5)	C33–C34	1.358 (9)	C48–C49	1.397 (6)
C3–C4	1.372 (8)	C19–C24	1.411 (5)	C34–C35	1.344 (10)	C50–C51	1.413 (6)
C4–C5	1.375 (8)	C19–P2	1.825 (4)	C35–C36	1.383 (7)	C50–C55	1.431 (6)
C5–C6	1.403 (7)	C20–C21	1.408 (7)	C37–C38	1.477 (5)	C50–P3	1.850 (4)
C7–C8	1.399 (5)	C21–C22	1.347 (8)	C37–C49	1.493 (5)	C51–C52	1.402 (6)
C7–C12	1.386 (5)	C22–C23	1.367 (7)	C37–P3	1.814 (4)	C51–C56	1.513 (6e
C7–P1	1.825 (4)	C23–C24	1.376 (6)	C38–C39	1.391 (6)	C52–C53	1.380 (8)
C8–C9	1.385 (5)	C25–C26	1.419 (6)	C38–C43	1.411 (5)	C53–C54	1.420 (8)
C9–C10	1.366 (6)	C25–C30	1.365 (6)	C39–C40	1.399 (6)	C54–C55	1.382 (7)
C10–C11	1.377 (6)	C25–P2	1.842 (4)	C40–C41	1.399 (7)	C55–C57	1.515 (7)
C11–C12	1.397 (6)	C26–C27	1.409 (8)	C41–C42	1.382 (7)		

Bond Angles

C37–Pt1–P1	100.51 (14)	C15–C16–C17	119.8 (6)	Pt1–C37–C38	114.4 (3)	C51–C50–P3	119.6 (4)
C37–Pt1–P2	160.54 (12)	C16–C17–C18	121.4 (6)	Pt1–C37–C49	117.8 (3)	C55–C50–P3	121.6 (4)
C37–Pt1–P3	47.28 (14)	C13–C18–C17	118.2 (5)	Pt1–C37–P3	72.58 (20)	C50–C51–C52	121.0 (5)
P1–Pt1–P2	98.92 (5)	C20–C19–C24	117.9 (4)	C38–C37–C49	104.2 (4)	C50–C51–C56	121.6 (4)
P1–Pt1–P3	146.67 (4)	C20–C19–P2	119.7 (4)	C38–C37–P3	128.1 (3)	C52–C51–C56	117.0 (5)
P2–Pt1–P3	113.36 (5)	C24–C19–P2	122.3 (3)	C49–C37–P3	117.5 (3)	C51–C52–C53	119.2 (5)
C2–C1–C6	118.7 (5)	C19–C20–C21	119.2 (5)	C37–C38–C39	130.1 (4)	C52–C53–C54	120.4 (6)
C2–C1–P1	126.4 (3)	C20–C21–C22	121.8 (6)	C37–C38–C43	110.0 (4)	C53–C54–C55	120.3 (6)
C6–C1–P1	114.8 (4)	C21–C22–C23	119.5 (6)	C39–C38–C43	119.9 (4)	C50–C55–C54	119.5 (5)
C1–C2–C3	120.4 (5)	C22–C23–C24	120.9 (5)	C38–C39–C40	119.4 (5)	C50–C55–C57	122.6 (5)
C2–C3–C4	121.0 (5)	C19–C24–C23	120.6 (4)	C39–C40–C41	119.8 (5)	C54–C55–C57	117.7 (6)
C3–C4–C5	11.8 (6)	C26–C25–C30	119.5 (5)	C40–C41–C42	121.2 (5)	Pt1–P1–C1	110.38 (16)
C4–C5–C6	119.7 (6)	C26–C25–P2	119.3 (4)	C41–C42–C43	119.1 (5)	Pt1–P1–C7	113.67 (15)
C1–C6–C5	120.3 (5)	C30–C25–P2	121.2 (4)	C38–C43–C42	120.7 (4)	Pt1–P1–C13	120.56 (16)
C8–C7–C12	118.4 (4)	C25–C26–C27	117.5 (5)	C38–C43–C44	107.9 (4)	C1–P1–C7	109.91 (23)
C8–C7–P1	117.3 (3)	C26–C27–C28	122.0 (6)	C42–C43–C44	131.3 (4)	C1–P1–C13	101.2 (3)
C12–C7–P1	124.2 (3)	C27–C28–C29	118.7 (7)	C43–C44–C45	131.1 (4)	C7–P1–C13	100.00 (24)
C7–C8–C9	120.1 (4)	C28–C29–C30	122.3 (7)	C43–C44–C49	108.9 (4)	Pt1–P2–C19	114.92 (15)
C8–C9–C10	120.7 (4)	C25–C30–C29	120.0 (6)	C45–C44–C49	120.0 (4)	Pt1–P2–C25	119.08 (15)
C9–C10–C11	120.4 (5)	C32–C31–C36	116.4 (6)	C44–C45–C46	118.0 (5)	Pt1–P2–C31	113.47 (17)
C10–C11–C12	119.3 (5)	C32–C31–P2	121.2 (4)	C45–C46–C47	122.0 (6)	C19–P2–C25	101.4 (3)
C7–C12–C11	120.9 (4)	C36–C31–P2	122.4 (4)	C46–C47–C48	120.0 (5)	C19–P2–C31	105.51 (24)
C14–C13–C18	120.1 (5)	C31–C32–C33	121.1 (5)	C47–C48–C49	119.7 (5)	C25–P2–C31	100.50 (25)
C14–C13–P1	119.0 (4)	C32–C33–C34	122.7 (7)	C37–C49–C44	108.8 (4)	Pt1–P3–C37	60.14 (15)
C18–C13–P1	120.8 (4)	C33–C34–C35	117.0 (8)	C37–C49–C48	130.9 (4)	Pt1–P3–C50	116.65 (16)
C13–C14–C15	119.1 (5)	C34–C35–C36	121.7 (7)	C44–C49–C48	120.3 (4)	C37–P3–C50	108.02 (25
C14–C15–C16	121.1 (6)	C31–C36–C35	120.9 (6)	C51–C50–C55	118.2 (4)		

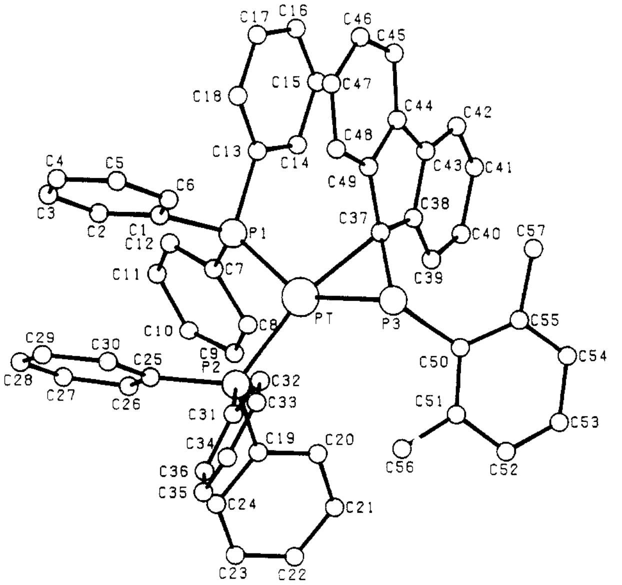

Figure 1. PLUTO drawing and numbering scheme of [Pt^0(PPh$_3$)$_2$(C$_{12}$H$_8$C=PC$_6$H$_3$Me$_2$-*o*,*o*′)] (**6**).

Other important criteria, which provide information about the extent of the interaction between the phosphaalkene unit and the Pt^0(PPh$_3$)$_2$ entity, are the changes of P–C bond length upon coordination and of the P–Pt–P angle. As compared with the P–C bond in the free phosphaalkene **2**,[1b] this bond has been substantially lengthened (about 0.1 Å) to a value of 1.814 (4) Å (see also Table V) which is typical for a P–C single bond (cf. the mean P–C(phenyl) bond length in **6** of 1.834 Å). Furthermore, the P(1)–Pt–P(2) angle is decreased upon η^2-coordination to a small value of 98.92 (5)°.

Discussion

In our previous analysis[2c] of the equilibrium composition of the η^1- and η^2-complexes Pt(PPh$_3$)$_2$(MesP=CPh$_2$) (**1a** and **1b**, respectively) in toluene, we showed that the η^2-complex **1b** is favored at low temperature by its lower enthalpy although the difference was found to be small: ^{31}P NMR (−70 °C) **1a**:**1b** = 11:89. At higher temperatures the more positive entropy (see eq 1) favors the η^1-coordination mode: ^{31}P NMR (5 °C) **1a**:**1b** = 60:40.

The new complexes Pt(PCy$_3$)$_2$(η^1-XylP=CPh$_2$) (4) and Pt(PPh$_3$)$_2$(η^2-C$_{12}$H$_8$C=PXyl) (**6**) are each representatives of one of the two extremes in the above-mentioned $\eta^1 \rightleftharpoons \eta^2$ equilibrium. The compounds show the spectroscopic data for the respective bonding modes in question, and no indications have been found that in solution similar

Table V. Some Selected Structural Data of η^1- and η^2-Heteroolefin Metal Complexes

compd	M-P^a	P-C^a	L-M-L^b	C-P-C^c
MesP=CPh$_2$ (**2**)		1.692 (3)		107.5
Pt(PPh$_3$)$_2$(η^1-MesP=CPh$_2$) (**1a**)	2.218 (3)	1.65 (1)	121.9 (1)	108.5 (5)
Cr(CO)$_5$[η^1-(MesP=CPh$_2$)]	2.356 (1)	1.679 (4)		109.8 (2)
Pt(PPh$_3$)$_2$(η^1-C$_{12}$H$_8$C=PXyl) (**6**)	2.356 (1)	1.814 (4)	98.92 (5)	108.0 (0)
Ni(bpy)[η^2-XylP=CPh$_2$)]^c	2.177 (2)	1.832 (6)	83.2 (2)	102.6 (3)
Ni(PMe$_3$)$_2$[η^2-(Me$_3$Si)$_2$CHP=C(SiMe$_3$)$_2$]^d	2.239 (2)	1.773 (8)	102.1 (1)	110.3 (4)
Pt(PPh$_3$)$_2$(η^2-C$_{12}$H$_8$CSO)^e (**7**)	2.313 (1)^k	1.762 (5)^f	106.42 (5)	113.9 (3)^g
Pt(PPh$_3$)$_2$(η^2-MesN=S=O)^h (**9**)	2.332 (4)^k	1.63 (1)^i	103.1 (1)	116.4 (7)^j

^{a} In Å. ^{b} In deg. ^{c} See ref 2e. ^{d} See ref 2f. ^{e} See ref 7b. ^{f} Value for C=S. ^{g} Value for C=S=O. ^{h} See ref 7c. ^{i} Value for N=S. ^{j} Value for N=S=O. ^{k} Value for Pt—S.

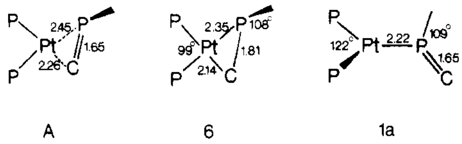

Figure 2. Geometry used in the theoretical analysis of Pt(PH$_3$)$_2$(HP=CH$_2$)^{2c} (A) and the actual geometries of **6** and **1a** as found by X-ray structure determination (for precise data, see Table IV) (distances in Å).

equilibria as found for **1** exist for **4** and **6**.[8]

The structure of **6** shows that the actual Pt—P and Pt—C distances are different indeed because the P=C bond is unsymmetrical and also that they both are much shorter than anticipated in our theoretical model Pt(PPh$_3$)$_2$(HP=CH$_2$) (see A in Figure 2).^{2c} More importantly, it is observed that (i) the P—C bond is substantially lengthened by the η^2-coordination (from ca. 1.69 to 1.81 Å), although the validity of this conclusion is somewhat restricted by the fact that the actual P=C bond length in the free ligand **5** is unknown and (ii) η^2-coordination is accompanied by a small P-Pt-P interligand bond angle of 98.92 (5)° between the PPh$_3$ ligands. A crystal structure of **4** is not available, but on the basis of the spectroscopic data it seems plausible to assume that in this complex the phosphaalkene XylP=CPh$_2$ similarly is η^1-coordinated as has been found for the phosphaalkene ligand in Pt(PPh$_3$)$_2$(η^1-MesP=CPh$_2$) (**1a**).

For the present discussion it is important to have a reasonable estimate for the minimum value of the Cy$_3$P-Pt-PCy$_3$ interligand bond angle. On the basis of the PCy$_3$ cone angle, which is expected in the range of 164–177°,[9] the latter interligand bond angle must be expected to be much larger than the ideal value of 120° in a trigonal species. Indeed, in Pt(PCy$_3$)$_2$(η^1-SO$_2$)^{10a} and Pt(PCy$_3$)$_2$,^{10b} which both contain a Pt(PCy$_3$)$_2$ unit, P-Pt-P interligand bond angles of 165.72° and 160.5°, respectively, have been found. The angle of 120° has only been found in the special case of Pt(PCy$_3$)$_3$.[11] The structure of the latter complex showed that this value can only be attained by intermeshing of the cyclohexyl groups which minimized the interligand repulsions.

In order to arrive at a more general picture of the factors determining η^1- or η^2-coordination of phosphaalkenes to M^{0}L$_2$ units, we have collected the available structural data in Table V.

Comparison of the data of the L$_2$M phosphaalkene complexes reveals that each bonding mode, η^1 or η^2, has its own specific set of interligand bond distances and angles (cf. Figure 2): (i) The η^1-bonding mode is characterized by Pt-P bond distances of about 2.25 Å. The P=C bond of the phosphaalkene unit is in the same range as that of the free ligand (1.692 (3) Å^{1b}), although it appears to be slightly, but consistently shorter: 1.65 (1) Å in Pt(PPh$_3$)$_2$(MesP=CPh$_2$) (**1a**),^{1c} 1.660 (9) Å in *cis*-PtCl$_2$(PEt$_3$)(MesP=CPh$_2$),^{2b} and 1.679 (4) Å in Cr(CO)$_5$(MesP=CPh$_2$).^{2a} This bond shortening in the η^1-bonding mode can be explained by electron transfer from the phosphorus lone pair of MesP=CPh$_2$ to platinum because the lone pair is antibonding with regard to the P=C bonding (cf. Figure 3 in ref 2c); probably this shortening effect of the P=C bond on coordination of the phosphaalkene ligand is partially compensated by the opposite lengthening effect brought about by electron donation from the Pt d$_{xz}$ orbital into the π^* orbital of MesP=CPh$_2$ (**2**).^{2c} Finally, in the η^1-complex **1a** the L-Pt-L bond angle for the PPh$_3$ coligands (121.9 (1)°) is close to the ideal interligand bond angles of 120° in trigonal arrangements. (ii) The η^2-bonding mode has as characteristic features the longer M—P bond length (cf. the Pt-P bond length in **6** is 2.356 (1) Å), the elongated P=C bond length in the phosphaalkene, and the acute L—M—L interligand bond angles between the coligands (PR$_3$, bpy).

To answer the question concerning the role which steric factors are playing in the phosphaalkene bonding mode to PtL$_2$, we consider first the influence of the L-Pt-L bond angle on the frontier orbital of this fragment. Recently, a series of computational studies were reported[12] concerning the frontier orbitals that are active in oxidative-addition processes of ML$_2$ fragments on, e.g., H$_2$ or CH$_4$. Previous experimental results^{7b,13} already suggested that the reactivity of, for example, PtL$_2$ fragments in oxidative-addition processes depend on both the L-Pt-L (L = phosphine) interligand bond angle and the steric size and basicity of the phosphine ligand. In a recent computational study Morokuma et al.^{12b} showed the interplay of these factors in the formation of *cis*-Pt(H)$_2$(PH$_3$)$_2$ from Pt(PH$_3$)$_2$ and H$_2$. The Pt-H and Pt-P bond strengths in the *cis*-Pt(H)$_2$(PH$_3$)$_2$ were studied as a function of the P-Pt-P interligand bond angle. It appeared that the Pt-H bond strength increased by about 10 kcal/mol for a decrease of the P-Pt-P interligand bond angle by 10° in the range 140–100°. An opposite dependence was found for the Pt-P bond strength. It was concluded that the decrease of the

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(8) UV-vis spectra of **1** in 2-methyltetrahydrofuran showed that the bands at 420 and 460 nm decrease in intensity on cooling. This is in accord with the observation that at lower temperature the **1a** $\rightleftharpoons$ **1b** equilibrium shifts to the η^2-coordination product **1b**.

(9) (a) A cone angle for PCy$_3$ of 179° was derived from models: Tolman, C. A. *Chem. Rev.* **1977**, 313; *J. Am. Chem. Soc.* **1970**, *92*, 2956. Later cone angle and ligand profile calculations on PCy$_3$ revealed cone angle estimates of 164° for the crowded ligand in Pt(PCy$_3$)$_3$^{10b} up to 177° for the uncrowded ligand in [Hg(SCN)$_2$(PCy$_3$)]$_n$.^{9b} (b) Ferguson, G.; Roberts, P. J.; Alyea, E. C.; Khan, M. *Inorg. Chem.* **1978**, *17*, 2965.

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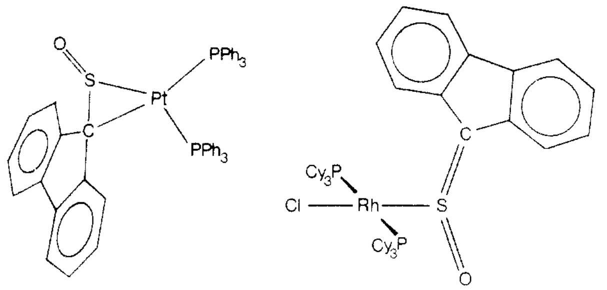

Figure 3. η^1- and η^2-bonding in related sulfinyl metal complexes depending on the type of metal–ligand fragment used.

P–Pt–P interligand bond angles activates efficiently and selectively one of the metal d orbitals, which transfers electrons to the reactant H_2 to the effect that the Pt–H bonds are strengthened.

This theoretical result can be used for the interpretation of our experimental results concerning the η^1-/η^2-bonding modes of phosphaalkenes to PtL_2 fragments. It appears that the above-mentioned d_{xz} orbital, which is sensitive to the L–Pt–L bond angle, in our theoretical analysis of the $Pt(PH_3)_2(H_2C{=}PH)$ model system[2c] is the orbital which likewise is responsible for the transfer of electrons from the metal via π-back-donation into the π^* orbital of the P=C bond in both the η^1- and η^2-bonding mode. In the $Pt(PH_3)_2(H_2C{=}PH)$ model system the effect of the π-back-donation ($\eta^2 >> \eta^1$) overcompensates only slightly that of σ-donation (lone pair in η^1 > that in η^2). However, in this theoretical analysis the influence of a variation of the P–Pt–P interligand bond angle on the delicate balance between η^1- and η^2-coordination was not taken into account. It is particularly the successful synthesis of **4** and **6** by changing the nature of either of the coligands (phosphines; **1a** vs. **4**) or the phosphaalkene (**1b** vs **6**) that points to the importance of the interligand bond angle on the relative stability of the η^1- and η^2-bonding modes. From the study of the $Pt(PH_3)_2$–H_2 oxidative-addition reaction it can be deduced that the larger interligand bond angle imposed by the change from PPh_3 in $Pt(PPh_3)_2(MesP{=}CPh_2)$ to the sterically more demanding PCy_3 ligands in **4** stabilizes the d_{xz} orbital of the PtL_2 fragment to the effect that the π-back-donation component in the Pt···P=C interaction decreases. Accordingly the σ-donation component, which dominates the η^1-bonding mode, becomes more important than the π-bonding component resulting in the stabilization of the η^1-bonding mode.

Alternatively, the η^2-bonding mode can be stabilized when the P–Pt–P interligand bond angle is reduced to about 100° (vide supra for the $Pt(PH_3)_2$–H_2 system) resulting in extensive electron transfer from the destabilized Pt d_{xz} into the π^* P=C. These values around 100° have been realized in the $Pt(PPh_3)_2(C_{12}H_8C{=}PPh_2)$ complex **6** and in $Ni(PMe_3)_2[\eta^2\text{-}(Me_3Si)_2CHP{=}C(SiMe_3)_2]$ while in $Ni(bpy)(\eta^2\text{-}XylP{=}CPh_2)$ an acute N–Ni–N angle of 83.2° is present as a result of the bite angle of the bpy chelate. It is the latter complex that also combines the smallest L–M–L interligand bond angle with the largest P=C bond lengthening (to 1.832 (6) Å) which indicates that the π-back-bonding components contributes extensively in the Ni···P=C interaction to the extent that this complex can be considered as a nickelaphosphacyclopropane with a single P—C bond rather than a Ni^0–phosphaalkene complex.

When the $Pt(PPh_3)_2$ unit is kept constant (**1b**, **6**), but the relative accessibility of the σ-P and π-P=C is influenced by a change in the phosphaalkene stereochemistry likewise, this η^1-/η^2-balance is disturbed. In the case of the ligand $C_{12}H_8C{=}PXyl$ (**5**), the η^1-bonding mode is energetically less favorable than, for example, that for $MesP{=}CPh_2$ (**2**), because of the repulsion between the fluorene-[H(1) or H(8)] and the $Pt(PPh_3)_2$ unit in the η^1-complex.

The rationale presented above can be extended to the interpretation of the bonding between M^0L_2 units and other heteroolefinic bonds. In Table V the relevant structural features of complexes with a $Pt(PPh_3)_2$ unit with either a sulfinyl (**7**) or a sulfinylaniline (**9**) are given. In both complexes η^2-coordination occurs, i.e., between Pt^0 and C=S (**7**) and Pt^0 and N=S (**9**), respectively. Similar arguments as outlined above can explain the preference of the η^2-bonding mode found for these complexes over the η^1-Pt–S one. Moreover, we have shown that the sulfinyl $C_{12}H_8C{=}S{=}O$, which has similar structural features as the phosphaalkene **5**, can be forced into the η^1-S coordination mode by changing the metal fragment from $Pt(PPh_3)_2$ to a T-shaped *trans*-$RhCl(PCy_3)_2$ (see Figure 3). In the latter compound the $C_{12}H_8C{=}SO$ ligand with its flat stereochemistry fits only between the mutually trans-positioned PCy_3 ligands when it is coordinated in the η^1-S-bonding mode.[13b]

Acknowledgment. Thanks are due to Professor Dr. E. J. Baerends for fruitful discussions.

Registry No. 4, 103240-45-5; 6, 89934-20-3; $Pt(COD)_2$, 12130-66-4; $[Pt(PPh_3)_2C_2H_4]$, 12120-15-9.

Supplementary Material Available: Tables of hydrogen atom coordinates (calculated) and anisotropic thermal parameters for all non-hydrogen atoms of **6** as well as an ORTEP plot (40% probability) (4 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.