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Stabilized Bis-ylides as a Source of Carbene Ligands in Palladium(II) and Platinum(II) Complexes

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The reaction of the α-stabilized bis-ylide $[Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3]$ with M(II) bis-solvato derivatives, *cis*-$[M(C_6F_5)_2(OC_4H_8)_2]$ or $[M(C{\wedge}X)(OC_4H_8)_2]ClO_4$ (M = Pd, Pt; $C{\wedge}X$ = orthometalated ligand), yields the ylide-carbene complexes *cis*-$[M(C_6F_5)_2\{C(CO_2Me){-}C(CO_2Me)(PPh_3)\}(PPh_3)]$ (M = Pt **1a**, Pd **1b**) or $[M(C{\wedge}X)\{C(CO_2Me){-}C(CO_2Me)(PPh_3)\}(PPh_3)]ClO_4$ (M = Pt, $C{\wedge}X$ = *o*-$CH_2C_6H_4P$(*o*-tolyl)$_2$, **2**; M = Pd, $C{\wedge}X$ = *o*-$CH_2C_6H_4P$(*o*-tolyl)$_2$, **3**; $CH_2C_9H_6N$-C^8,N, **4**; NC_5H_4-*o*-C_6H_4, **5**; $C_{13}H_8N$, **6**). The reaction appears to proceed with P=C bond cleavage, generating a carbene-ylide ligand $[{:}C(CO_2Me){-}C(CO_2Me)PPh_3]$ and a PPh_3 group, both coordinated to the metal center. The reaction of the solvato complexes $[M(C{\wedge}X)(OC_4H_8)(PPh_3)]ClO_4$ with the bis-ylide results in the selective formation of $[M(C{\wedge}X)(PPh_3)_2]ClO_4$ (M = Pt, $C{\wedge}X$ = *o*-$CH_2C_6H_4P$(*o*-tolyl)$_2$, **7**; M = Pd, $C{\wedge}X$ = $CH_2C_9H_6N$-C^8,N, **8**), showing that when one vacant position is available, only the PPh_3 group binds to the metal center, and the carbene fragment decomposes to $O{=}PPh_3$ and dimethylfumarate. On the other hand, the reaction of the bis-solvato precursors $[Pd(C_6F_5)(L)(OC_4H_8)_2]ClO_4$ with the bis-ylide yields the corresponding metallacyclopropane [Pd{*trans*-*C*(C_6F_5)(CO_2Me)−*C*(PPh_3)(CO_2Me)}(L)(PPh_3)](ClO_4) (L = SC_4H_8, **9**; PPh_3, **10**), probably through the initial formation of an ylide-carbene complex—similar to **1**−**6**—followed by the migratory insertion of the carbene ligand into the Pd−C(C_6F_5) bond and coordination of the newly generated ylide function. The crystal structure of complex **1a**·CH_2Cl_2 has been analyzed by X-ray diffraction.

Introduction

In the course of our ongoing research on the coordination chemistry of stabilized bis-ylide ligands, we have developed synthetic strategies through which, starting from bis-phosphonium salts $[Ph_3PCH_2C(O)CH_2PPh_3]^{2+}$ or ylide-phosphonium salts $[Ph_3P{=}CHC(O)CH_2PPh_3]^+$, it has been possible to obtain C,C-bonded bis-ylides,[1] to promote C−H bond activations[2−5] and also to synthesize different types of homo- and heteropolynuclear systems.[6] The versatility shown by this type of system has prompted us to expand our present studies on the coordinating properties of phosphorus ylides to other, related bis-ylide ligands, and we have now focused our attention on the doubly stabilized bis-ylide $Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3$ (see Figure 1), in which the two ylidic carbons are adjacent to each other and each one is stabilized through the presence of a carbonyl oxygen. This bis-ylide is a yellow solid, stable for short periods of time when exposed to oxygen or moisture, and easily prepared in multigram quantities by reaction of dimethylacetylenedicarboxylate with an excess of PPh_3 in dry Et_2O.[7] Extensive work has been done on the synthesis of this bis-ylide and related compounds,[8] but only from a purely synthetic organic point of view, and no reports have appeared concerning its coordinating properties toward transition metals.

However, the reactivity of this ligand toward Pd(II) and Pt(II) substrates has been unexpectedly extensive and interesting, to the point that we have found at least four different reactivity patterns, as a function of the starting material, all of them sharing an initial P=C bond cleavage in one of the ylide groups, resulting in the generation of two fragments: a PPh_3 ligand and the ylide carbene $:C(CO_2Me){-}C(CO_2Me){=}PPh_3$. Although the P−C bond activation process is already known, most of the available data relate to P−C bond activation in PPh_n fragments, giving rise to Ph and PPh_{n-1} units.[9] One of the most striking examples of this type of

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(1) Falvello, L. R.; Fernández, S.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Inorg. Chem.* **1998**, *37*, 6007.

(2) Falvello, L. R.; Fernández, S.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1998**, *17*, 5887.

(3) Falvello, L. R.; Fernández, S.; Larraz, C.; Llusar, R.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2001**, *20*, 1424.

(4) Larraz, C.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **2000**, *24*, 623.

(5) Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **2000**, *602*, 151.

(6) Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chem.* **1999**, *38*, 2455.

(7) (a) Shaw, M. A.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. (C)* **1967**, 2442. (b) Kolodiazhnyi, O. I. *Phosphorus Ylides, Chemistry and Application in Organic Synthesis*; Wiley-VCH: Weinheim, 1999; p 49, and references therein.

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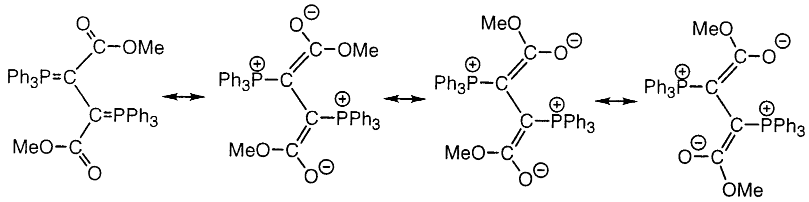


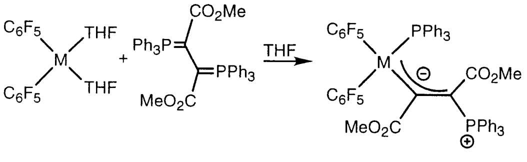
Figure 1. Resonance forms for the bis-ylide.

activation is the synthesis of phenyl derivatives of Ni(II) with phosphino-enolate ligands from the reaction of $Ni^0(COD)_2$ (COD = 1,5-cyclooctadiene) with the stabilized ylide $Ph_3P{=}C(H)C(O)Ph$.[10,11] The reactivity that we report here is formally different, since the bis-ylide behaves as a genuine carbene transfer agent in the synthesis of complexes with ylide-carbene ligands. The synthesis of complexes with ylide-carbene ligands is reported in the literature, but following different routes: (i) the reaction between metal carbonyls and strong nucleophilic ylides;[12] (ii) phosphine-alkyne couplings promoted by transition metals,[13] sometimes described as alkyne insertions into the metal−phosphorus bond; and (iii) intramolecular nucleophilic attack of nonstabilized ylides to coordinated nitriles.[14] On the other hand, there are very few examples reported in which an ylide acts as a genuine carbene transfer agent, and in these cases, a nonstabilized ylide is involved.[15]

In this contribution we report the use of stabilized bis-ylides as carbene transfer reagents in the synthesis of ylide-carbene complexes and, in some cases, their further reactivity.

Results and Discussion

1. Synthesis of Ylide-Carbene Complexes. The reaction of the bis-solvato derivative $[Pt(C_6F_5)_2(THF)_2]$ with the bis-ylide $Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3$ (1:1 molar ratio, THF, rt 30 min) gives, after solvent evaporation and Et_2O addition, the ylide-carbene complex *cis*-$[Pt(C_6F_5)_2\{C(CO_2Me){-}C(PPh_3)(CO_2Me)\}(PPh_3)]$, **1a**, as a white solid, stable to air and moisture at room temperature. In a similar process, $[Pd(C_6F_5)_2(THF)_2]$ reacts with the bis-ylide, under the same experimental conditions, affording *cis*-$[Pd(C_6F_5)_2\{C(CO_2Me){-}C(PPh_3)(CO_2Me)\}(PPh_3)]$, **1b** (eq 1). Both complexes show correct elemental analyses and mass spectra, suggesting the incorporation of one bis-ylide unit for each $[M(C_6F_5)_2]$ fragment. Complex **1a** crystallizes as colorless block-shape crystals, adequate for X-ray purposes, by slow diffusion of Et_2O vapor into a CH_2Cl_2 solution of the crude complex.



M = Pt (**1a**); Pd (**1b**)

(1)

X-ray analysis of **1a**·CH_2Cl_2 (monoclinic, space group $P2_1/c$) reveals the presence of two independent molecules in the asymmetric unit. A drawing of one of the two molecules is presented in Figure 2. Relevant crystallographic parameters concerning the data acquisition and structure solution and refinement are given in Table 1 and in the Experimental Section, and selected

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(8) (a) Shaw, M. A.; Ward, R. S. In *Topics in Phosphorus Chemistry*; Griffith, E. J., Grayson, M., Eds.; Interscience Publishers: John Wiley and Sons: New York, 1972; Vol. 7, pp 1−32. (b) Johnson, A. W.; Tebby, J. C. *J. Chem. Soc.* **1961**, 2126. (c) Allen, D.; Tebby, J. C.; Williams, D. H. *Tetrahedron Lett.* **1965**, *28*, 2361. (d) Shaw, M. A.; Tebby, J. C.; Ronayne, J.; Williams, D. H. *J. Chem. Soc. (C)* **1967**, 944. (e) Shaw, M. A.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. (C)* **1968**, 1609. (f) Shaw, M. A.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. (C)* **1968**, 2795. (g) Waite, N. E.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. (C)* **1969**, 1100. (h) Richards, E. M.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. (C)* **1969**, 1542. (i) Shaw, M. A.; Tebby, J. C. *J. Chem. Soc. (C)* **1970**, 5. (j) Waite, N. E.; Tebby, J. C. *J. Chem Soc. (C)* **1970**, 386. (k) Shaw, M. A.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. (C)* **1970**, 504. (l) Richards, E. M.; Tebby, J. C. *J. Chem. Soc. (C)* **1971**, 1059. (m) Richards, E. M.; Tebby, J. C. *J. Chem. Soc. (C)* **1971**, 1064. (n) Waite, N. E.; Tebby, J. C.; Ward, R. S.; Shaw, M. A.; Williams, D. H. *J. Chem. Soc. (C)* **1971**, 1620. (o) Wilson, I. F.; Tebby, J. C. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2830. (p) Butterfield, P. J.; Tebby, J. C.; Griffiths, V. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1189. (q) Tebby, J. C.; Wilson, I. F.; Griffiths, V. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2133.

(9) (a) Kwong, F. Y.; Chan, K. S. *Organometallics* **2001**, *20*, 2570. (b) Kwong, F. K.; Lai, C. W.; Chan, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8864. (c) de la Torre, G.; Gouloumis, A.; Vázquez, P.; Torres, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2895. (d) Kwong, F. K.; Chan, K. S. *Organometallics* **2000**, *19*, 2058. (e) Kwong, F. Y.; Chan, K. S. *Chem. Commun.* **2000**, 1069. (f) Cabeza, J. A.; Martínez-García, M. A.; Riera, V.; Ardura, D.; García-Granda, S. *Eur. J. Inorg. Chem.* **2000**, 499. (g) Bandini, A. L.; Banditelli, G.; Minghetti, G. *J. Organomet. Chem.* **2000**, *595*, 224. (h) Viñas, C.; Núñez, R.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. *Organometallics* **1999**, *18*, 4712. (i) Bender, R.; Bouaoud, S.-E.; Braunstein, P.; Dusausoy, Y.; Merabet, N.; Raya, J.; Rouag, D. *J. Chem. Soc., Dalton Trans.* **1999**, 735. (j) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 481. (k) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441. (l) Crochet, P.; Demerseman, B.; Rocaboy, C.; Schleyer, D. *Organometallics* **1996**, *15*, 3048. (m) Kong, K. C.; Cheng, C. H. *J. Am. Chem. Soc.* **1991**, *113*, 6313. (n) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

(10) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466.

(11) Johnson, A. W.; Kaska, W. C.; Ostoja Starzewski, K. A.; Dixon, D. A. *Ylides and Imines of Phosphorus*; John Wiley & Sons: New York, 1993; Chapter 14, and references therein.

(12) (a) Malisch, W.; Blau, H.; Voran, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 780. (b) Voran, S.; Blau, H.; Malisch, W.; Schubert, U. *J. Organomet. Chem.* **1982**, *232*, C33. (c) Malisch, W.; Blau, H.; Schubert, U. *Chem. Ber.* **1983**, *116*, 690. (d) Neumüller, B.; Riffel, H.; Fluck, E. *Z. Anorg. Allg. Chem.* **1990**, *588*, 147. (e) Petz, W.; Weller, F.; Schmock, F. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1123.

(13) (a) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Chechulina, I. N.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1982**, *238*, 223. (b) Lappas, D.; Hoffman, D. M.; Folting, K.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 587. (c) Hoffman, D. M.; Huffman, J. C.; Lappas, D.; Wierda, D. A. *Organometallics* **1993**, *12*, 4312. Related examples: (d) Allen, A.; Lin, W. *Organometallics* **1999**, *18*, 2922. (e) Chin, C. S.; Lee, M.; Oh, M.; Won, G.; Kim, M.; Park, Y. J. *Organometallics* **2000**, *19*, 1572, and references therein.

(14) (a) Facchin, G.; Campostrini, R.; Michelin, R. A. *J. Organomet. Chem.* **1985**, *294*, C21. (b) Michelin, R. A.; Facchin, G.; Braga, D.; Sabatino, P. *Organometallics* **1986**, *5*, 2265. (c) Michelin, R. A.; Mozzon, M.; Facchin, G.; Braga, D.; Sabatino, P. *J. Chem. Soc., Dalton Trans.* **1988**, 1803.

(15) (a) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43 (Ta). (b) Schwartz, J. *Pure Appl. Chem.* **1980**, *52*, 733 (Zr). (c) Korswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1049 (Fe). (d) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952 (Ta). (e) Gandelman, M.; Rybtchinsky, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 5372 (Rh, Ru, Os).

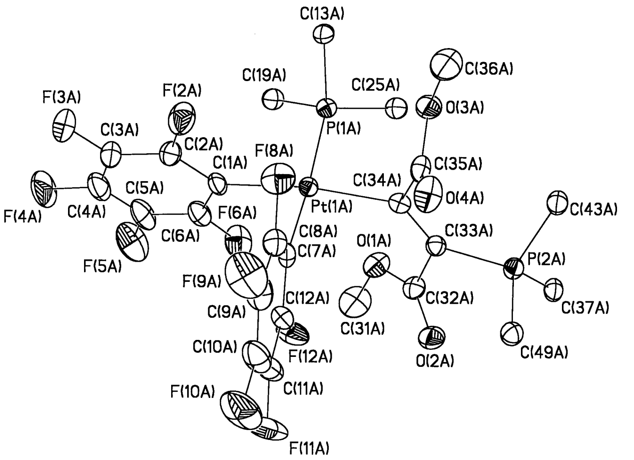

Figure 2. Thermal ellipsoid plot of molecule A of complex **1a**. Phenyl groups (except C_{ipso}) and H atoms have been omitted for clarity. Non-hydrogen atoms are drawn at the 30% probability level.

Table 1. Crystal Data and Structure Refinement for $1a\cdot CH_2Cl_2$

formula	$[C_{55}H_{36}Cl_2F_{10}O_4P_2Pt]$
mol wt	1278.77
data collection *T*, K	297(2)
λ, Å	0.71073
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	21.338(6)
b, Å	13.216(4)
c, Å	37.126(10)
β, deg	102.248(6)
V, Å^3	10231(5)
Z	8
D_{calc}, Mg m^{-3}	1.660
μ (Mo Kα), mm^{-1}	2.993
F(000)	5040
cryst size, mm	0.228 × 0.108 × 0.103
θ range, deg	0.98−27.48
no. of reflns collected/unique	71858/23443 [R_{int} = 0.0484]
no. of data/restraints/params	23443/66/1374
GOF	1.022
R indices [$I > 2\sigma(I)$]^a	R1 = 0.0391, wR2 = 0.0875
R indices (all data)^a	R1 = 0.0853, wR2 = 0.1045
largest peak, hole, e·Å^{-3}	1.202, −1.535

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $GOF = [\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

bond distances and angles are collected in Table 2. The two molecules show essentially identical bond distances and angles, with differences arising in the relative orientations of phenyl and carbomethoxy groups. In each molecule, the platinum atom is located in a slightly distorted square-planar environment, bonded to the ipso carbon atoms of the C_6F_5 ligands, to the P atom of the PPh_3 group, and to the carbenic carbon atom of the ylide-carbene ligand. Thus, it is clear that the reaction occurs with activation of one of the P−C bonds in the starting bis-ylide, generation of the PPh_3 and $:C(CO_2Me){-}C(CO_2Me)(PPh_3)$ groups, and coordination of these resulting fragments in mutually *cis* positions after displacement of the THF molecules (see eq 1).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $1a\cdot CH_2Cl_2$

	molecule A	molecule B
Pt(1)−C(34)	2.056(5)	2.047(5)
Pt(1)−C(1)	2.076(5)	2.083(5)
Pt(1)−C(7)	2.079(5)	2.071(5)
Pt(1)−P(1)	2.3019(14)	2.2999(15)
O(1)−C(32)	1.319(6)	1.287(8)
P(2)−C(33)	1.810(5)	1.818(5)
O(2)−C(32)	1.200(6)	1.231(8)
O(3)−C(35)	1.333(6)	1.332(6)
O(4)−C(35)	1.197(6)	1.211(6)
C(32)−C(33)	1.489(7)	1.508(8)
C(33)−C(34)	1.339(6)	1.345(7)
C(34)−C(35)	1.490(7)	1.475(7)
C(34)−Pt(1)−C(7)	85.78(18)	86.09(19)
C(1)−Pt(1)−C(7)	87.44(19)	86.90(19)
C(34)−Pt(1)−P(1)	96.07(14)	95.96(14)
C(1)−Pt(1)−P(1)	91.25(15)	91.40(14)
O(2)−C(32)−O(1)	123.9(5)	124.9(6)
O(2)−C(32)−C(33)	121.6(5)	119.5(6)
O(1)−C(32)−C(33)	114.5(4)	115.5(6)
C(34)−C(33)−C(32)	123.3(4)	123.5(5)
C(34)−C(33)−P(2)	125.8(4)	125.3(4)
C(32)−C(33)−P(2)	110.0(3)	110.2(4)
C(33)−C(34)−C(35)	119.6(4)	120.2(4)
C(33)−C(34)−Pt(1)	128.3(4)	126.4(4)
C(35)−C(34)−Pt(1)	110.5(3)	112.0(3)
O(4)−C(35)−O(3)	124.6(5)	124.1(5)
O(4)−C(35)−C(34)	123.2(5)	123.1(5)
O(3)−C(35)−C(34)	112.2(5)	112.6(5)
C(49)−P(2)−C(33)	110.5(2)	110.7(2)
C(37)−P(2)−C(33)	108.1(2)	111.2(2)

The Pt−C(C_6F_5) bond distances [2.076(5), 2.079(5), 2.071(5), and 2.083(5) Å] are identical, within experimental error, and fall in the usual range of distances found for this type of bond.[16] The Pt−C(carbene) bond distances Pt(1A)−C(34A) [2.056(5) Å] and Pt(1B)−C(34B) [2.047(5) Å] are also identical, within experimental error. The comparison of these bond distances with those found in related platinum-carbene complexes, in which the carbene ligand is located *trans* to another carbon atom [range 2.00(2)−2.079(13) Å],[17] shows that this Pt−C bond has some double-bond character. Moreover, these bond distances fall near the lower limit of the range of distances found for Pt−C(sp^2) bonds *trans* to another carbon atom; for instance, the range is 2.043(13)−2.104(5) Å in Pt−C(phenyl) derivatives.[17] In addition, the C−C bond distances C(33A)−C(34A) [1.339(6) Å] and C(33B)−C(34B) [1.345(7) Å] are slightly longer than those usually found for olefinic C(sp^2)−C(sp^2) bonds [range 1.326−1.331 Å] and very nearly equal to the mean value found from unconjugated C═C−C═O systems [1.330(8) Å],[18] but are clearly shorter than the C(sp^2)−C(sp^2) single bonds found in the same molecule, for instance, C(34A)−C(35A) [1.490(7) Å], C(32A)−C(33A) [1.489(7) Å], C(34B)−C(35B) [1.475(7) Å], and C(32B)−C(33B) [1.508(8) Å]. The multiple-bond character of the C(33A)−C(34A) and C(33B)−C(34B) bonds is also reflected in the values found for the bond angles around C(34A) (sum of angles: 358.4°), C(33A) (359.2°), C(34B) (358.6°), and C(33B) (359.0°) and in the dihedral angles Pt(1A)−C(34A)−C(33A)−P(2A) [−167.3(5)°], Pt(1A)−C(34A)−C(33A)−C(32A) [0.6(5)°], Pt(1B)−C(34B)−C(33B)−P(2B) [167.2(5)°], and Pt(1B)−C(34B)−C(33B)−C(32B) [−1.0-

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(16) Falvello, L. R.; Forniés, J.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 309.

(17) (a) Hartley, F. R. In *Comprehensive Organometallic Chemistry I*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Editors-in-chief; Pergamon Press: Oxford, 1982. Vol. 6, p 502 and ff. (b) Pruchnik, F. P. In *Organometallic Chemistry of the Transition Elements*; Plenum Press: 1990; Chapter 5, p 277 and ff.

(18) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 685. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; 1995; Vol. C., Table 9.5, pp 685−706.

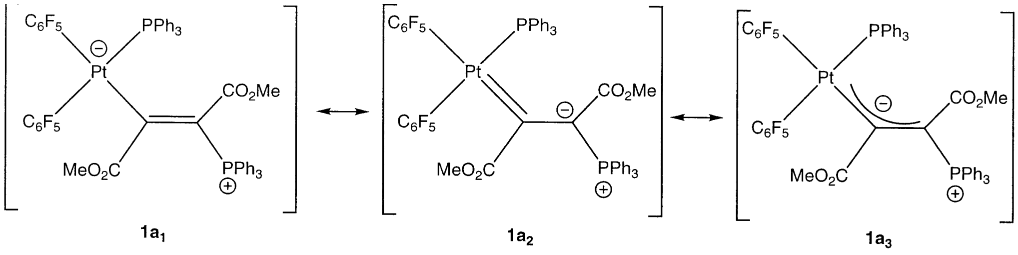

Figure 3. Resonance forms for complex **1a**.

(5)°]. The planarity of the fragments Pt(1)−C(34)−C(33)−P(2) (A and B) can also be observed in the deviations of their component atoms with respect to the best least-squares planes (maximum 0.08 and 0.09 Å, respectively). Moreover, these planar fragments Pt−C−C−P are nearly perpendicular to the coordination plane (calculated using Pt(1)−P(1)−C(1)−C(7)−C(34), A and B), the dihedral angles between the respective best least-squares planes being, respectively, 84.1(5)° and 88.2(6)°.

The P(2A)−C bond distances are identical, within experimental error [and the same is true for the bond distances P(2B)−C], and all of them are longer than those expected for an ylidic P═C bond, even in the case of stabilized ylides (average value 1.71 Å).[11] This fact implies that the P−C bonds do not possess multiple-bond character, that they are not involved in any process of charge delocalization, and, consequently, that the environment around the phosphorus atom is that of a phosphonium moiety. Moreover, the carbomethoxide groups are not involved in any charge delocalization, as can be seen from the C═O bond distances C(35A)−O(4A) [1.197(6) Å], C(32A)−O(2A) [1.200(6) Å], C(35B)−O(4B) [1.211(6) Å], and C(32B)−O(2B) [1.231(8) Å], typical for carbonyl groups.[18]

In summary, the Pt−C_α and the C_α−C_β bond distances show multiple bond character, but no other bond is involved in charge delocalization. In Figure 3 we have represented the limiting resonant forms inferred from the X-ray data (**1a₁** and **1a₂**). Between the two limiting structures, it is sensible to assume that the form **1a₁** predominates in the bonding description, since the $P^+\cdots C^-$ interaction in **1a₂** would be inconsistent with the long P−C_β bond distances found. Very similar bonding descriptions have been reported in the literature for Re,[13b,c] Cr, Mo, and W,[12b] Mn,[12c,13a] and Pt[14] derivatives. In all cases the authors suggest that the vinyl structure best represent the bonding mode, with a small contribution (but not negligible) of the ylide-carbene form.

The spectroscopic characterization of **1a** and **1b** provides additional structural information. The IR spectra of these complexes show typical bands due to the presence of *cis*-C_6F_5 ligands[16] and strong carbonyl absorptions at 1698 cm^{-1} (**1a**) and 1699 cm^{-1} (**1b**). The positions of the carbonyl bands show that these groups are not involved in charge delocalization processes since, in that case, this absorption should appear at lower energies. For instance, the CO stretch in the starting bis-ylide[7] appears at 1598 cm^{-1} and in the resonance-stabilized P-ylide $Ph_3P{=}C(H)CO_2Me$ at 1621 cm^{-1}.[19] The ^1H NMR spectra of **1a** and **1b** are very similar and show signals corresponding to the aromatic protons and to the carbomethoxy groups. The ^{19}F NMR spectra show signals typical of organometallic C_6F_5 ligands (see Experimental Section). In the F_{ortho} region (−116 ppm for **1a** and −112 ppm for **1b**), it is possible to observe four different peaks, corresponding to the four F_{ortho} nuclei present in the molecule. This fact implies that (i) the two C_6F_5 groups are chemically inequivalent, since the *trans* ligands are different; (ii) the molecular plane is not a symmetry plane, due to the asymmetry imposed by the carbene ligand; and (iii) the two C_6F_5 groups and the carbene ligand are not able to rotate freely around the M−C bond, probably due to the presence of the bulky PPh_3 ligand and the carbene. Meanwhile, the $^{31}P\{^1H\}$ NMR spectra of **1a** and **1b** show clearly the presence of two different P atoms in each compound. For **1a** the signals are easily assigned, due to the presence of ^{195}Pt satellites: the PPh_3 ligand appears at 14.27 ppm ($^1J_{Pt-P} = 2725$ Hz) and the P atom of the ylide carbene appears at 16.50 ppm ($^3J_{Pt-P} = 265$ Hz). In the case of **1b** the PPh_3 ligand appears at 20.85 ppm (broadened by the presence of the *trans*-C_6F_5 ligand) and the P atom of the ylide carbene appears at 13.42 ppm (sharp singlet). The positions of the resonances attributed to the P atom of the carbene ligand are very near to those found for resonance-stabilized ylides,[11] showing that the form **1a₂** does actually contribute to the bonding description.

The $^{13}C\{^1H\}$ NMR spectrum of **1a** is particularly informative. The resonance attributed to the carbenic carbon atom (C_α) in the group Pt−C_α−C_β−P appears at 214.71 ppm ($^1J_{Pt-C} = 665$ Hz), showing unambiguously its carbenic nature and the contribution of the canonical form **1a₂** to the bonding description. The chemical shift values for carbenic carbons appear in the range 170−330 ppm,[20] but the main body of data appear between 200 and 250 ppm, with values of the coupling constant $^1J_{Pt-C}$ in the range 700−1100 Hz.[20] On the other hand, the chemical shift values for the C_α in vinyl derivatives of Pt(II) appear in the range 110−190 ppm, high-field shifted with respect to the values found for carbene derivatives.[20] As we can see, the values observed for **1a** clearly show the carbenic nature of the C_α carbon atom. The carbonyl groups appear as doublets at 171.77 ppm ($^3J_{PC} = 15.1$ Hz) and at 168.66 ppm ($^2J_{PC} = 24.3$ Hz), the signal attributed to the C_β appears at 110.21 ppm ($^1J_{PC} = 73.4$ Hz, $^3J_{PC} = 1.9$ Hz), and the OMe carbons appear at 52.45 and 50.42 ppm, in addition to the expected resonances due to the Ph groups and the C_6F_5 ligands, the latter showing very low intensity.

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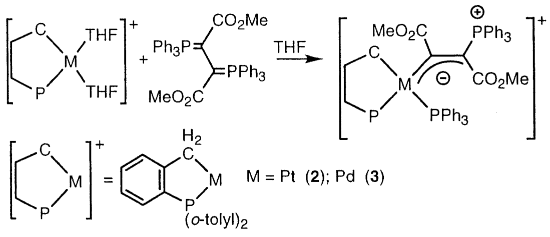
(19) Isler, O.; Gutmann, H.; Montavon, M.; Ruegg, R.; Ryser, G.; Zeller, P. *Helv. Chim. Acta* **1957**, *40,* 1242.

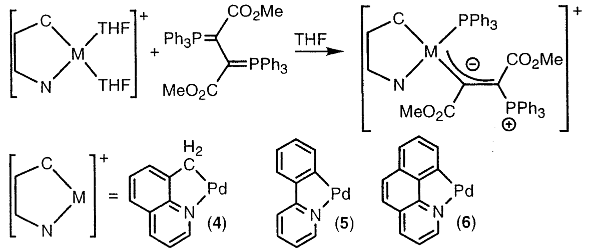
(20) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; pp 141−142.

Due to the singularity of this reaction—a stabilized bis-ylide as a carbene transfer reagent—we have carried out a series of reactions, changing the starting material (neutral vs cationic; Pd vs Pt) and the number of available positions (bis-solvato vs mono-solvato) in order to check the generality of the process.

Several orthometalated, cationic, bis-solvato derivatives have been allowed to react with the bis-ylide $[Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3]$. The bis-solvato complexes were prepared by reaction of the corresponding orthometalated $[M(C{\wedge}X)(\mu\text{-hal})]_2$ derivatives with $AgClO_4$ (1:2 molar ratio, THF, rt) followed by removal of the silver halide by filtration. The freshly prepared solutions of $[M(C{\wedge}X)(THF)_2]ClO_4$ react with the bis-ylide (1:1 molar ratio, THF, rt), yielding the new carbene complexes $[M(C{\wedge}X)\{C(CO_2Me){-}C(CO_2Me)(PPh_3)\}(PPh_3)]ClO_4$ ($C{\wedge}X = o\text{-}CH_2C_6H_4P(o\text{-tolyl})_2$, M = Pt, **2**; M = Pd, **3**; M = Pd, $C{\wedge}X = CH_2C_9H_6N\text{-}C^8,N$, **4**; $NC_5H_4\text{-}o\text{-}C_6H_4$, **5**; $C_{13}H_8N$, **6**) as air-stable solids (see schematic diagrams of complexes **2**−**6** in eqs 2.1 and 2.2). The analytical data and mass spectra of **2**−**6** are in good agreement with the incorporation of a bis-ylide to each $[M(C{\wedge}X)]ClO_4$ fragment.



(2.1)



(2.2)

The spectroscopic characterization of **2**−**6** shows unambiguously that each of these compounds also contains a PPh_3 group and a carbene ligand and that a similar P−C bond activation process could be involved here. The IR spectra of **2**−**6** show strong absorptions in the 1700 cm^{-1} region, attributed to the carbonyl stretch. The particular position in each complex varies slightly from one to another [range 1693−1724 cm^{-1}], but all of them fall in the same region as that described for **1a** and **1b**, suggesting a similar environment.

The NMR spectra of **2**−**6** show only one set of resonances in each spectrum, showing that each complex appears as a single isomer. Due to the asymmetric nature of the metalated ligands and the different electronic and steric requirements of the donor atoms bonded to the metal, one could expect, at first glance, the formation of different isomers, either geometric (*cis*/*trans*) or conformational isomers, arising from the relative disposition of the carbomethoxy groups around the $C_\alpha{-}C_\beta$ bond (*Z*/*E*). In the crystal structure of **1a** we see that the configuration of the two CO_2Me groups around the C−C bond is *E*. Assuming that this arrangement is preserved in complexes **2**−**6**, only geometric isomers should be considered.

In the case of complexes **2** and **3** (see eq 2.1), their geometry is clearly inferred from the $^{31}P\{^1H\}$ NMR spectra. The spectrum of **2** shows three signals, each as a doublet of doublets with ^{195}Pt satellites. The resonance attributed to the orthometalated P atom appears at 28.25 ppm ($^4J_{PP}$ = 35.3 Hz, $^2J_{PPcis}$ = 14.8 Hz, $^1J_{PtP}$ = 2519 Hz), the signal assigned to the PPh_3 ligand at 18.95 ppm ($^4J_{PP}$ = 5.6 Hz, $^2J_{PPcis}$ = 14.8 Hz, $^1J_{PtP}$ = 2056 Hz), and that due to the $-C(PPh_3)$ group at 15.57 ppm ($^4J_{PP}$ = 35.3 Hz, $^4J_{PP}$ = 5.6 Hz, $^3J_{PPt}$ = 305 Hz). The small value of the $^2J_{PP}$ coupling constant shows clearly that the two coordinated P atoms are mutually *cis*, since a P-*trans*-to-P arrangement is reflected in typical $^2J_{PP}$ values of about 450 Hz.[21] Similar conclusions can be derived from the $^{31}P\{^1H\}$ NMR spectrum of **3**. Furthermore, the ^1H NMR spectra of **2** and **3** show, in addition to the phenyl, CO_2Me, and Me(tolyl) resonances, signals assigned to the diastereotopic $M{-}CH_2$ protons, which appear as an AB spin system coupled with ^{31}P. This fact implies that the metalated CH_2 group and the PPh_3 ligand are located mutually *trans* and, as has been described for **1a** and **1b**, that the molecular plane is not a symmetry plane due to the restricted rotation of the carbene ligand around the M−C bond.

The $^{13}C\{^1H\}$ NMR spectrum of **2** shows a signal at 217.21 ppm, attributed to the carbene C_α atom, as a doublet of doublets ($^2J_{PtransC}$ = 109 Hz, $^2J_{PC}$ = 8.5 Hz), in keeping with the P-*trans*-to-C arrangement. As expected, the signal assigned to the metalated methylene appears at 37.09 ppm as a doublet ($^2J_{PtransC}$ = 87.1 Hz), and the C_β atom appears as a doublet of doublets ($^1J_{PC}$ = 70.9 Hz, $^3J_{PC}$ = 2.7 Hz). Similar conclusions can be inferred from the analysis of the NMR spectra of **3**, although in this case we have not been able to observe the signals due to the C_α and C_β atoms, even with long accumulations. On the basis of all these data, we propose the structures shown in eq 2.1 for **2** and **3**.

In the case of complexes **4**−**6**, the formation of the carbene ligands can be clearly seen from the analysis of the $^{13}C\{^1H\}$ NMR spectra. In fact, signals at 220.69 ppm (dd, J_{PC} = 14.1 Hz, J_{PC} = 10.2 Hz, **5**) and at 219.67 ppm (dd, J_{PC} = 13.1 Hz, J_{PC} = 9.9 Hz, **6**) are attributable to C_α of the carbene ligand. In addition, C_β appears at 110.06 ppm (d, $^1J_{PC}$ = 77.4 Hz, **5**) and at 110.14 ppm (dd, $^1J_{PC}$ = 71.2 Hz, $^3J_{PC}$ = 3.8 Hz, **6**), and it is also possible to observe signals corresponding to the different orthometalated ligands (see Experimental Section). Moreover, the $^{31}P\{^1H\}$ NMR spectra of **4**−**6** show two signals in all cases, corresponding to the presence of the two different types of P atoms, and the ^1H NMR spectra show the presence of all the expected resonances. With respect to the ligand arrangements in complexes **4**−**6**, we propose the structure shown in eq 2.2, that is, the PPh_3 ligand *trans* to the N atom, on the basis of the known aversion of the PPh_3 ligand to be coordinated *trans* to an aryl C atom (*transphobia*).[22] This works well for the aryl complexes **5** (*ortho*-phenylpyridine) and **6** (benzo[*h*]quinoline), where there are no reports of or-

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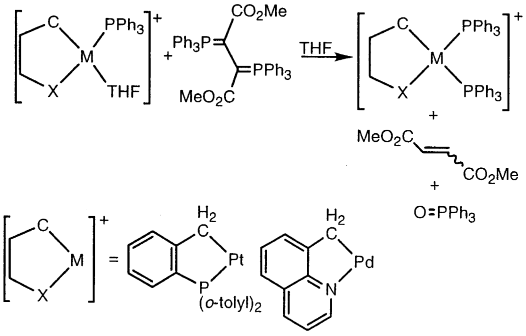
(21) Fernández, S.; García, M. M.; Navarro, R. Urriolabeitia, E. P. *J. Organomet. Chem.* **1998**, *561*, 67.

thopalladated complexes containing the P-*trans*-C arrangement. For complex **4** this proposal is also sustainable due to the observation, in the $^{13}C\{^1H\}$ NMR spectrum, of a signal at 38.55 ppm (attributed to the Pd-CH_2 atom) with triplet structure ($J_{PC} = 5.1$ Hz). The small value of the coupling constant could be due to the coupling with the *cis* P atom and with the remote P atom of the *trans* carbene ligand.

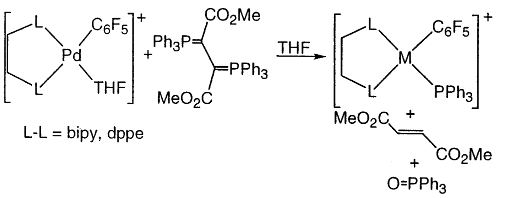
In summary, neutral or cationic bis-solvato derivatives of Pd(II) and Pt(II) with strongly coordinated ancillary ligands are able to promote, under very mild conditions, one P−C bond cleavage in the α-stabilized bis-ylide $Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3$, generating two fragments—PPh_3 and the ylide-carbene [:$C(CO_2Me){-}C(CO_2Me)PPh_3$]—which in turn coordinate to the metal center.

2. Reactions of the Bis-ylide with Mono-solvated Species. Further extension of the work developed in Section 1 arises from the question, What happens when only one position is available? Since in the P=C bond activation process two ligands with very different electronic and steric requirements are formed—and with quite different metal-to-ligand bond energies—a selective coordination of only one of the two fragments can be anticipated. Some examples are presented as schematic diagrams in eqs 3, 4, and 5.

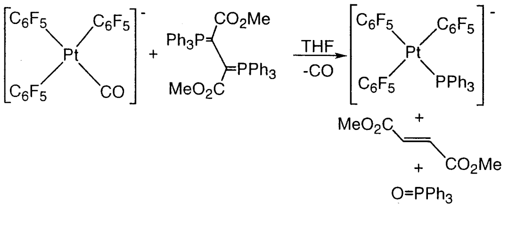


(3)

(**7**) (**8**)



(4)



(5)

The reaction of the solvato derivatives [M(C∧X)(THF)(PPh_3)]ClO_4—obtained from the corresponding halo-derivatives by abstraction of the halide with $AgClO_4$ (see Experimental Section)—with the bis-ylide (1:1 molar ratio, dry THF, rt) affords, after the usual workup, the bis-phosphino complexes [M(C∧X)$(PPh_3)_2$]ClO_4, (M = Pt, C∧X = *o*-$CH_2C_6H_4P$(*o*-tolyl)$_2$, **7**; M = Pd, C∧X = $CH_2C_9H_6N{-}C^8$,N, **8**) following the process described in eq 3. These bis-phosphino derivatives are isolated from the reaction mixture by THF evaporation and Et_2O addition. The evaporation of the ether solution gives an oily residue, which can be characterized spectroscopically as a mixture of O=PPh_3 and dimethylfumarate (scant amounts of the isomeric dimethylmaleate were detected in some experiments). Complexes **7** and **8** give satisfactory elemental analyses and mass spectra in accord with the proposed structure. The incorporation of a PPh_3 ligand into the starting solvato complex is clearly inferred from the $^{31}P\{^1H\}$ NMR spectra of **7** and **8**. Thus, the spectrum of **7** shows the presence of three different resonances, corresponding to the three inequivalent P atoms present in the molecule, while the spectrum of **8** shows the two signals expected (see Experimental Section).

In the same way, the reaction of the solvato derivatives [Pd(C_6F_5)(L−L)(THF)]ClO_4 with the bis-ylide (1:1 molar ratio, dry THF, rt) affords the phosphino complexes [Pd(C_6F_5)(L−L)(PPh_3)]ClO_4 (L−L = 2,2′-bipyridine; $Ph_2PCH_2CH_2PPh_2$) as per the process reported in eq 4, and the reaction of (NBu_4)[Pt$(C_6F_5)_3$(CO)] with the bis-ylide, under the same reaction conditions, gives (NBu_4)[Pt$(C_6F_5)_3$(PPh_3)], as presented in eq 5. These complexes have been isolated from the reaction mixtures after solvent evaporation and Et_2O addition, and characterized as described previously.[23] As expected, the spectroscopic characterization of the residue obtained after evaporation of the ether solution showed it to be a mixture of O=PPh_3 and dimethylfumarate.

In light of these facts, it seems that the reaction of the monosolvato complexes with the bis-ylide also occurs through P=C bond activation and generation of the PPh_3 ligand and the carbene fragment. However, only the PPh_3 ligand remains coordinated to the metal center, affording the corresponding phosphino derivatives, while the carbene ligand decomposes, probably due to reaction with water, giving O=PPh_3 and dimethylfumarate. This decomposition of the carbene fragment has already been reported in the literature,[7a] and the presence of water could be due to the exposure of the reaction mixture to air at the end of the reaction. In an attempt to trap the carbene ligand, the reaction of [Pt(THF)($CH_2C_6H_4$-*o*-P(*o*-tol)$_2$)(PPh_3)]ClO_4 with the bis-ylide was carried out in strictly anhydrous conditions and in the presence of an excess of styrene. In this reaction, complex **7** was again obtained; however none of the anticipated cyclopropanation product was obtained.

Some questions about the synthesis of **1**−**8** arise at this point: (i) How is the P=C bond activation produced; (ii) how is the PPh_3 fragment transferred to the metal center; and (iii) is it an inter- or intramolecular transfer?

The answer to the first question can be inferred easily from the reported hydrolysis of this bis-ylide.[7a] This hydrolysis (in boiling water) generates equimolecular amounts of PPh_3, O=PPh_3, and dimethyl fumarate, through an initial protonation of one of the ylidic units, expulsion of the PPh_3 fragment, and hydrolysis of the resulting vinyl phosphonium salt. In line with this, it is reasonable to assume that in our reaction the first step is the C-bonding of the bis-ylide to the metal center

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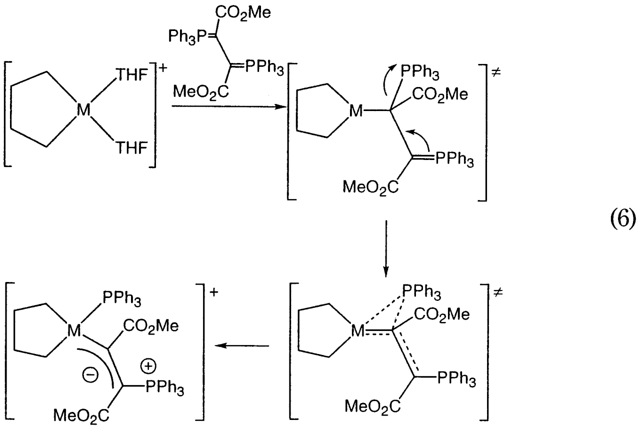
(22) (a) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. (b) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez-de-Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066.

(23) Usón, R.; Forniés, J. *Adv. Organomet. Chem.* **1988**, *28*, 219, and references therein.

(a Lewis acid) (see eq 6). After this coordination, the electron density remaining in the remote, nonbonded ylide could be delocalized through the $C_\beta-C_\alpha-M$ system, promoting the 1,2-shift of the PPh_3 group from the C_α to the metal. This latter shift can be explained in terms of the Lewis acid nature of the metal, taking into account the high affinity of the metal (Pd, Pt) for phosphine ligands. Thus, it seems that the presence of the second, “remote” ylide unit is decisive in achieving the P=C bond activation in the first.



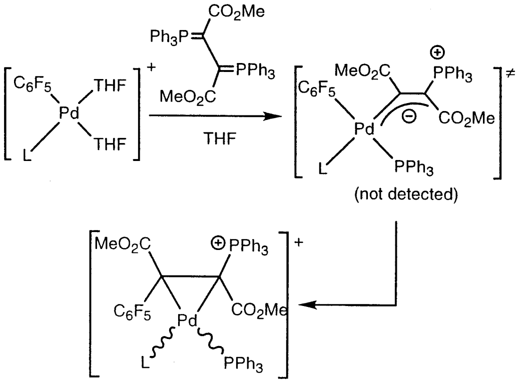
(6)

The process proposed in eq 6 seems to involve an intramolecular transfer of the PPh_3 group from C_α to the metal. We have discarded the hypothesis of an intermolecular transfer of PPh_3 since, in that case, free PPh_3 should be present in the reaction medium. This free PPh_3 would be able to react with other species present in the solution, for instance the starting bis-solvato derivatives, giving bis-phosphino complexes. This side reaction would be more likely to occur in the early stages of the reaction, when the concentration of the bis-solvato complexes is high. However, we have not detected the formation of bis-phosphino derivatives in the syntheses of **1**−**6**. Moreover, we have carried out the reaction of the bis-solvate $Pt(C_6F_5)_2(THF)_2$ with the bis-ylide in molar ratio 2:1, that is, in the presence of an excess of solvato complex, using the same experimental workup as that described for **1a**. The first fraction, insoluble in Et_2O, was identified as pure **1a**; the second one, insoluble in *n*-hexane, was identified as $Pt(C_6F_5)_2(THF)_2$, and we have not detected the presence of $Pt(C_6F_5)_2(PPh_3)_2$, even at trace levels.

This reaction scheme also helps explain why in the case of monosolvato starting compounds only the bis-phosphino complexes **7** and **8** were obtained. Since only one coordination site is available, the ligand with the highest bond formation energy remains coordinated. The syntheses of **7** and **8** through a 1,2-shift of the PPh_3 group from the coordinated C_α to the metal center and elimination (probably at the same time) of the carbene fragment also imputes an intramolecular (rather than intermolecular) migration of the PPh_3. An intermolecular mechanism for the synthesis of **8** would be formally equivalent to the reaction of **4** with PPh_3, and, in fact, complex **4** does not react with PPh_3 in THF at room temperature.

3. Migratory Insertion Reactions. Synthesis of Metallacyclopropane Complexes. In the syntheses of **1**−**6** we have used as starting materials neutral bis-solvato complexes with two monodentate, monoanionic, ligands (C_6F_5) or cationic bis-solvato derivatives with chelating monoanionic ligands. The reactivity of cationic bis-solvato precursors with two monodentate ligands, one neutral and one anionic (SC_4H_8 = tht, PPh_3, and C_6F_5), toward the bis-ylide results in the synthesis of a new type of compound.

The intermediate bis-solvato complexes $[Pd(C_6F_5)(L)(THF)_2]ClO_4$ (L = tht, PPh_3) were prepared by reaction of the corresponding halide-bridged dinuclear complexes with $AgClO_4$ (1:2 molar ratio) in THF at room temperature. After removal of the AgCl, the freshly prepared solutions were allowed to react with the bis-ylide (Pd/bis-ylide = 1:1), giving, after a few minutes, yellow solutions. The reaction products were isolated either by direct precipitation in THF (L = tht, **9**) or by removal of the solvent and Et_2O addition (L = PPh_3, **10**). Complexes **9** and **10** have been characterized spectroscopically as the metallacyclopropane derivatives shown in eq 7 on the basis of the following observations.



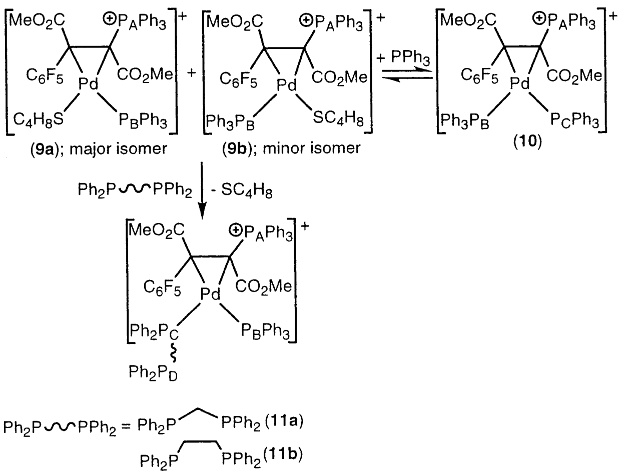
L = SC_4H_8 (**9**), PPh_3 (**10**)

(7)

The elemental analyses of **9** and **10** are in good agreement with the incorporation of one bis-ylide unit to each $[Pd(C_6F_5)(L)(ClO_4)]$ fragment. However, the spectroscopic characterization of **9** and **10** shows clearly that they are not ylide-carbene complexes analogous to **1**−**6**. The mass spectrum of **9** shows peaks at 939 amu, corresponding to the loss of the tht ligand, at 677 amu (loss of the tht and PPh_3 ligands) and at 571 amu (loss, in addition, of the Pd atom). All peaks show correct isotopic distributions. In fact, the isotopic distribution of the peak at 571 amu is in good agreement with that expected for the cation $[(C_6F_5)(C(CO_2Me)-C(CO_2Me)(PPh_3)]^+$, generated by addition of the C_6F_5 group to the ylide-carbene ligand, suggesting that the C_6F_5 group is no longer organometallic. The same conclusions can be derived from the mass spectrum of **10**.

The loss of the organometallic nature of the C_6F_5 fragment is also inferred from the IR spectra and, unambiguously, from the ^{19}F NMR spectra of **9** and **10**. In the IR spectra, the typical absorptions of metalated C_6F_5 groups (1630, 1500, 1060, 950, and 780 cm^{-1}) have been replaced by those characteristic of C_6F_5 bonded to a carbon atom (1650, 1515, 1490, 1130, 990, and 950 cm^{-1}),[24] although, due to the presence of the ClO_4 and CO_2Me groups, some absorptions appear overlapped. The ^{19}F NMR spectrum of **9** shows the presence of two set of signals, corresponding to the presence of two

Scheme 1



isomers (1:5 molar ratio), while that of **10** shows only one set of signals. Each set comprises five different peaks, corresponding to the five chemically inequivalent F atoms, thus showing that the C_6F_5 groups do not have free rotation around the C−Cipso(C_6F_5) bond. For complex **9** the signals attributed to the F_{ortho} nuclei appear between −131.35 and −136.29 ppm, shifted to high field more than 10 ppm with respect to the starting compound (−121.23 ppm for $[Pd(\mu\text{-}Cl)((C_6F_5)(tht)]_2)$ and in a region typical for C−C_6F_5 groups.[24] For **10** these signals appear between −129.9 and −131.3 ppm.

The assignment of the structures **9a** for the major isomer and **9b** for the minor isomer shown in Scheme 1 has been carried out through the analysis of the $^{31}P\{^1H\}$ NMR spectrum of **9**. The signals corresponding to the minor isomer **9b** appear as doublets at 29.08 ppm (P_A) and at 23.18 ppm (P_B) with $^3J_{PP} = 18.2$ Hz, while those corresponding to the major isomer **9a** appear as a singlet at 28.56 ppm (P_A) and a doublet at 25.92 ppm (P_B, $J = 26$ Hz). The pseudo-*trans* arrangement of the P atoms in **9b** could account for the observation of P−P coupling, which is not observed in **9a** due to their pseudo-*cis* disposition. Moreover, P_B in **9a** appears as a doublet and is arranged pseudo-*trans* with respect to the C_6F_5 group, as reflected in the coupling constant $J_{PF} = 26$ Hz, which also appears in the ^{19}F NMR spectrum. For the major isomer **9a**, one of the F_{ortho} signals (−134.04 ppm) appears as a doublet (J_{FF}), while the other (−134.25 ppm) appears as a triplet ($J_{PF} \approx J_{FF}$). As expected, the $^{31}P\{^1H\}$ NMR spectrum of **10** (see Scheme 1) shows three resonances. The signal at 29.97 ppm, attributed to P_A, appears as a doublet ($J_{AB} = 17.5$ Hz) due to the coupling with P_B, which appears at 23.22 ppm as a doublet of doublets ($J_{AB} = 17.5$ Hz, $J_{BC} = 26.0$ Hz). Also, the signal assigned to P_C appears as a triplet (instead of the expected doublet due to "only P−P coupling") due to the P_BP_C coupling and to the P_C−F_{ortho} coupling, which is once again observed in the ^{19}F NMR spectrum of **10** (signal at −131.30 ppm). Unfortunately, the resonances from the metalated C_α and C_β carbon atoms, which could have provided definitive proof of the incorporation of the C_6F_5 group into the ylide-carbene ligand, were not observed in the $^{13}C\{^1H\}$ NMR spectra of **9** and **10**, despite the utilization of long accumulation periods.

The synthesis of **9** and **10** can be understood as a formal migratory insertion of the carbene ligand into the Pd−C(C_6F_5) bond. It is reasonable to assume that the first step of the reaction is the P=C bond activation and the generation of the corresponding phosphino-(ylide-carbene) derivatives (see eq 7), analogous to complexes **1**−**6**, although in this case these intermediates could not be detected. These intermediates could be obtained, in principle, as a mixture of three isomers (C_6F_5 *cis* to carbene and *cis* to tht; C_6F_5 *cis* to carbene and *cis* to PPh_3; and C_6F_5 *trans* to carbene; see Scheme 2) with different populations in accord with their mutual *trans* influences.[22] The *cis* arrangement of the C_6F_5 and carbene ligands is a prerequisite to the migratory insertion process, while a *trans* configuration obviates this type of reaction.[25] However, since **9** is obtained as two isomers, it is reasonable to suppose that, either before or after the migratory insertion process, an isomerization process exchanges the positions of the tht and PPh_3 ligands; such isomerizations are not rare in Pd(II) complexes.[26]

In a second step, a migratory insertion reaction of the carbene ligand into the Pd−C(C_6F_5) bond takes place. This reaction can be seen either as migratory insertion or as nucleophilic attack of the C_6F_5 ligand, and both points of view are well documented in the literature for Pd(II) complexes.[24,27] This reaction is worthy of note, due to the remarkable stability of the M−C(C_6F_5) bonds,[23] which allow the synthesis of derivatives **1a** and **1b**, for instance. As a result of the migratory insertion process, the carbenic C_α atom becomes a σ-alkyl C atom (sp^3 hybridyzed), bonded to palladium, and also the pure ylide functionality is restored. The last step is simply the coordination of the ylidic carbon C_β at the vacant coordination site generated after the migration of the C_6F_5 group, in such a way that a metallacyclopropane derivative is obtained. Very few examples of metallacyclopropanes with phosphonium substituents have been reported in the literature.[28] This type of complex has been obtained through different synthetic routes, the main one being the nucleophilic attack (intra- or intermolecular) of a PR_3 group on a σ-vinyl ligand.[28a,d−g]

The labile tht ligand in the mixture **9** can easily be displaced from the coordination sphere of palladium by addition of other ligands. Thus, the addition of PPh_3 to a $CDCl_3$ solution of **9** (see Experimental Section) gives an equilibrium mixture between **9**, **10**, free tht, and PPh_3. When bidentate phosphines are used, such as dppm $[Ph_2PCH_2PPh_2]$ or dppe $[Ph_2PCH_2CH_2PPh_2]$, the new complexes **11a** (dppm) and **11b** (dppe) are obtained

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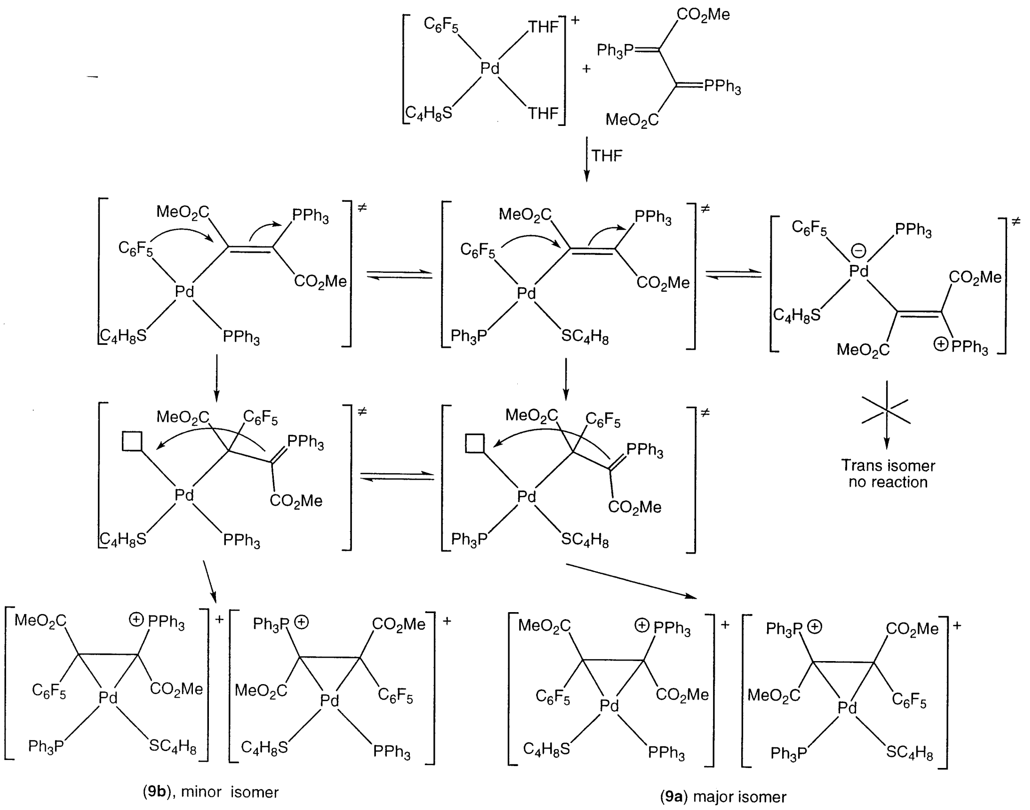
[24] (a) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079. (b) Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E.; Jones, P. E.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1982**, 2389.

[25] Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

[26] Minitti, D. *Inorg. Chem.* **1994**, *33*, 2631.

[27] (a) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Tetrahedron* **1998**, *54*, 13851. (b) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 5964. (c) Albéniz, A. C.; Casado, A. L.; Espinet, P. *Organometallics* **1997**, *16*, 5416. (d) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4138. (e) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4030. (f) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *J. Am. Chem. Soc.* **1996**, *118*, 7145. (g) Albéniz, A. C.; Espinet, P.; Lin, Y.-S.; Orpen, A. G.; Martín, A. *Organometallics* **1996**, *15*, 5003. (h) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1996**, *15*, 5010. (i) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1995**, *14*, 2977. (j) Albéniz, A. C.; Espinet, P. *J. Organomet. Chem.* **1993**, *452*, 229. (k) Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594.

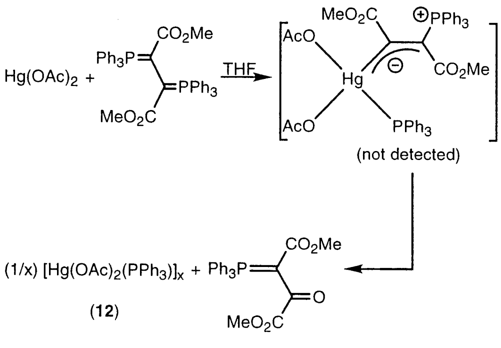
Scheme 2



(see Scheme 1), and, in this case, unreacted **9** was not detected. Complexes **11a** and **11b** were characterized only spectroscopically in CD_2Cl_2 solution. These complexes are rather unstable, and attempts to crystallize them from these solutions were unsuccessful, due to the formation of several unidentified species. The ^{19}F NMR spectra of **11a** and **11b** are very similar to those described for **9** and **10** and can be analyzed in the same terms. The $^{31}P\{^1H\}$ NMR spectra show four signals, corresponding to the expected four different P atoms. Three of these peaks appear in the low-field region, and the observed coupling pattern is very similar to that reported for **10**, while the remaining resonance appears at high field (−21.70 ppm for **11a**; −14.86 ppm for **11b**), clearly indicating the presence of a nonbonded P atom.

4. Reactivity of Hg(II) Complexes with the Bis-ylide. In the preceding paragraphs, we have reported the P=C bond activation in the bis-ylide $Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3$ promoted by electrophilic Pd(II) or Pt(II) complexes, giving carbene complexes, which can be stable or evolve in different ways. Prompted by the results obtained, we have begun to explore the reactivity of other metallic substrates with electrophilic natures toward the bis-ylide. Salts or simple complexes of Hg(II) could be considered as good candidates for starting materials, taking into account, moreover, that carbene complexes of Hg(II) are known and stable.[29] However, our first attempts using $HgCl_2$ or $HgPh_2$ (Ph = phenyl) were unsuccessful, and a mixture of the starting compounds was recovered after 24 h stirring at room temeparture.

When the starting compound is $Hg(OAc)_2$ (OAc = acetate), a new reaction takes place. A suspension of $Hg(OAc)_2$ in dry THF was allowed to react with the bis-ylide (1:1 molar ratio) for 24 h at room temperature under Ar atmosphere. After the reaction period, the solid in suspension was filtered and recrystallized from CH_2Cl_2/Et_2O, affording white crystals of **12** (see eq 8 and Experimental Section). The yield of **12**, based on



(8)

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[28] (a) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1989**, *8*, 967. (b) Alt, H. G.; Engelhardt, H. E.; Rogers, R. D. *J. Organomet. Chem.* **1989**, *362*, 117. (c) Alt, H. G.; Engelhardt, H. E.; Steinlein, E. *J. Organomet. Chem.* **1988**, *344*, 227. (d) Rybin, L. V.; Petrovskaya, E. A.; Rubinskaya, M. I.; Kuz'mina, L. G.; Struchkov, Yu. T.; Kaverin, V. V.; Koneva, N. Yu. *J. Organomet. Chem.* **1985**, *288*, 119. (e) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1984**, *3*, 1438. (f) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644. (g) Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchais, J. E.; L'Haridon, P. *Organometallics* **1983**, *2*, 1681.

[29] (a) Clark, A. M.; Oliver, A. G.; Rickard, C. E. F.; Wright, L. J.; Roper, W. R. *Acta Crystallogr., Sect. C* **2000**, *56*, 26. (b) Bildstein, B.; Malaun, M.; Kopacka, H.; Ongania, K.-H.; Wurst, K. *J. Organomet. Chem.* **1998**, *552*, 45, and references therein. (c) Luger, V. P.; Ruban, G. *Acta Crystallogr., Sect. B* **1971**, *27*, 2276. (d) Schöllkopf, U.; Gerhart, F. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 970. (e) Schöllkopf, U.; Gerhart, F. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 560.

Hg, is 39.6%. The THF solution was evaporated to dryness and the residue washed with Et_2O, giving a yellow solid characterized as a mixture of the starting compounds. Finally, white crystals of the stabilized ylide **13** (45.2% yield based on bis-ylide) were deposited from the ether solution after standing at room temperature for an additional 24 h. The yield of complex **12** with respect to the starting Hg derivative is more or less similar to that obtained for ylide **13** with respect to the starting bis-ylide. This fact shows that the reaction has not reached completion (45% conversion) and also that, even though the P=C bond activation has taken place, only the PPh_3 ligand remains bonded to the Hg center while the carbene fragment evolves in a different way from those reported above (mixtures of $O{=}PPh_3$ and dimethyl fumarate).

The characterization of complex **12** clearly reveals the presence of two acetate ligands and one PPh_3 group for each Hg atom, but we have not determined its nuclearity (this type of complex could be mono- or dinuclear).[30] Typical absorptions due to acetate (1582 cm^{-1}) and PPh_3 ligands (700–800 and 500 cm^{-1} regions) are observed in the IR spectrum of **12**, and the ^1H NMR spectrum shows signals attributed to Ph and Me groups, respectively, in 15:6 ratio. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance with ^{199}Hg satellites ($^1J_{HgP}$ = 8389 Hz), with this value of the coupling constant similar to those reported in related complexes.[31] The analytical and spectroscopic data for ylide **13** are in good agreement with the structure depicted in eq 8. Three strong absorptions can be seen in the carbonyl region: 1740 cm^{-1} (assigned to the CO fragment), 1671 cm^{-1} (COOMe terminal, not delocalized), and 1564 cm^{-1} (COOMe in resonance with the ylide function). The ^1H NMR spectrum displays the expected signals, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 16.60 ppm (typical for resonance stabilized ylides),[7,11] and the $^{13}C\{^1H\}$ NMR spectrum shows, among others, three signals in the carbonyl region [184.38 ppm (CO), 167.79 and 167.55 ppm (2 *C*OOMe)] and a doublet resonance at 68.04 ppm ($^1J_{PC}$ = 111.2 Hz) attributed to the ylidic carbon atom. Although there are numerous reports of doubly stabilized ylides with similar structures,[32] as far as we are aware the ylide **13** has not previously been reported.

Even if compounds **12** and **13** can be unambiguously characterized, the different reactivity observed in this case (synthesis of **13**) already suggests that the decomposition reaction of the carbene ligand could occur through different intermediates, in which the acetate ligand could play an important role. Further work in this area is in progress.

Conclusions

The P=C bond in the bis-ylide $Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3$ can be activated by a variety of electrophilic metal precursors, and this cleavage generates PPh_3 and the carbene $[{:}C(CO_2Me){-}C(CO_2Me)PPh_3]$. Different products can be obtained as a function of the starting material. The reaction with bis-solvato complexes of Pd(II) and Pt(II) gives products with both ligands coordinated to the metal center. In this synthesis of carbene complexes, the bis-ylide behaves as a genuine carbene transfer reagent. Moreover, in reactions with complexes with only one C_6F_5 ligand, a further migratory insertion reaction occurs and metallacyclopropane derivatives are obtained. When monosolvato species are used as precursors, the P=C bond activation promoted by the metal also occurs, but only the PPh_3 ligand remains coordinated and the carbene ligand decomposes. The synthetic potential of this facile and unexpected preparative method of carbene complexes as well as their reactivity and applications merit a detailed study, and further work in this area is currently in progress.

Experimental Section

Safety Note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution. See: *J. Chem. Ed.* **1973**, *50*, A335–A337.

General Methods. Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyzer. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. ^1H (300.13 MHz), ^{19}F (282.41 MHz), $^{13}C\{^1H\}$ (75.47 MHz), and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or DMSO-d_6 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard, while ^{19}F and $^{31}P\{^1H\}$ were externally referenced to $CFCl_3$ and H_3PO_4 (85%), respectively. Mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer.

***cis*-[Pt(C_6F_5)$_2$(PPh_3){C(CO_2Me)–C(PPh_3)(CO_2Me)}], 1a.** To a solution of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (0.181 g, 0.113 mmol) in THF (20 mL) was added $AgClO_4$ (0.047 g, 0.23 mmol). This mixture was stirred at room temperature with exclusion of light for 20 min, then the solvent was evaporated to dryness and the residue extracted with dry Et_2O (20 mL). After removal of the insoluble AgCl and NBu_4ClO_4, the ether solution—containing *cis*-$Pt(C_6F_5)_2(THF)_2$—was evaporated to dryness and the oily residue redissolved with dry THF (15 mL). The resulting solution was allowed to react with the bis-ylide $Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3$ (0.150 g, 0.225 mmol) for 3 h, giving a pale yellow solution. The evaporation of the solvent and treatment of the residue with Et_2O (10 mL) gives complex **1a** as a white solid, which was filtered, washed with additional Et_2O (10 mL), and air-dried. Obtained: 0.134 g (49.8% yield). Crystals of complex **1a** were obtained by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of the title complex. These crystals contain variable amounts of CH_2Cl_2 of crystallization.

Anal. Calcd for $[C_{54}H_{36}F_{10}O_4P_2Pt]\cdot 0.25CH_2Cl_2$: C, 53.53; H, 3.02. Found: C, 53.48; H, 3.27. MS (FAB+) [*m/z*, (%)]: 1196 (10%) [M^+], 1029 (80%) [$(M - C_6F_5)^+$]. IR (ν, cm^{-1}): 1698 ($\nu_{C=O}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.74–7.18 (m, 30H, Ph), 3.66 (s, 3H, OMe), 2.54 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 16.50 (s, $=C(PPh_3)$, $^3J_{Pt-P} = 265$ Hz), 14.27 (s, $Pt{-}PPh_3$, $^1J_{Pt-P} = 2725$ Hz). ^{19}F NMR (CD_2Cl_2, rt): δ (ppm), −115.98 (m, 1F, F_{ortho}, $^3J_{Pt-F} = 304$ Hz), −116.72 (m, 1F, F_{ortho}, $^3J_{Pt-F} = 315$ Hz), −116.92 (m, 1F, F_{ortho}, $^3J_{Pt-F} = 334$ Hz),

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[30] (a) Ferguson, G.; Alyea, E. C.; Khan, M.; Roberts, P. J.; Parvez, M. *Acta Crystallogr., Sect. A* **1978**, *34*, S128. (b) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Khan, M. A. *J. Chem. Res. (S)* **1979**, 360.

[31] Berger, S.; Braun, S.; Kalinowski, H.-O. In *NMR–Spektroskopie Von Nichtmetallen*: Georg Thieme Verlag: Stuttgart, 1993; Band 3, ^{31}P-NMR-Spektroskopie, p 172.

[32] Aitken, R. A.; Karodia, N.; Lightfoot, P. *J. Chem. Soc., Perkin Trans. 2* **2000**, 333.

−119.77 (m, 1F, F_{ortho}, $^3J_{Pt-F}$ = 304 Hz), −164.61 (t, 1F, F_{para}), −165.16 (m, 3F, $2F_{meta} + F_{para}$), −165.88 (m, 2F, F_{meta}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 214.71 (s, Pt=C, $^1J_{Pt-C}$ = 665.0 Hz), 171.77 (d, CO_2, $^3J_{PC}$ = 15.1 Hz), 168.66 (d, CO_2, $^2J_{PC}$ = 24.3 Hz), 148.82 (m, C_6F_5), 145.86 (m, C_6F_5), 138.15 (m, C_6F_5), 135.14 (d, C_{meta}, Ph, $^3J_{PC}$ = 10.7 Hz), 134.37 (d, C_{meta}, Ph, $^3J_{PC}$ = 10.1 Hz), 133.93 (d, C_{para}, Ph, $^4J_{PC}$ = 2.8 Hz), 132.84 (d, C_{ipso}, Ph, $^1J_{PC}$ = 50.9 Hz), 130.17 (d, C_{para}, Ph, $^4J_{PC}$ = 1.2 Hz), 129.35 (d, C_{ortho}, Ph, $^2J_{PC}$ = 12.7 Hz), 127.77 (d, C_{ortho}, Ph, $^2J_{PC}$ = 10.1 Hz), 120.93 (d, C_{ipso}, Ph, $^1J_{PC}$ = 88.1 Hz), 110.21 (dd, =C(P), $^1J_{PC}$ = 73.4 Hz, $^3J_{PC}$ = 1.9 Hz), 52.45 (s, OMe), 50.42 (s, OMe).

***cis*-[Pd(C₆F₅)₂(PPh₃){C(CO₂Me)−C(PPh₃)(CO₂Me)}], 1b.** Complex **1b** was prepared following the same experimental procedure as that described for **1a**. $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6F_5)_2]_2$ (0.144 g, 0.113 mmol) reacts in dry THF (20 mL) with $AgClO_4$ (0.047 g, 0.23 mmol) and $Ph_3P{=}C(CO_2Me){-}C(CO_2Me){=}PPh_3$ (0.150 g, 0.225 mmol) to give **1b** as a white solid. Obtained: 0.147 g (59.0% yield). Complex **1b** crystallizes as regular block-shaped colorless crystals by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of the crude product.

Anal. Calcd for $[C_{54}H_{36}F_{10}O_4P_2Pd]$: C, 58.58; H, 3.28. Found: C, 58.35; H, 3.11. MS (FAB+) [*m/z*, (%)]: 940 (10%) $[(M - C_6F_5 + H)^+]$, 773 (20%) $[(M - 2C_6F_5 + H^+]$, 677 (15%) $[(M - C_6F_5 - PPh_3)^+]$. IR (ν, cm^{-1}): 1696 ($\nu_{C=O}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.69−7.17 (m, 30H, Ph), 3.74 (s, 3H, OMe), 2.64 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 20.85 (s, Pd−PPh_3), 13.42 (s, =C(PPh_3)). ^{19}F NMR (CD_2Cl_2, rt): δ (ppm), −110.82 (m, 1F, F_{ortho}), −111.66 (m, 1F, F_{ortho}), −112.17 (m, 1F, F_{ortho}), −116.24 (m, 1F, F_{ortho}), −162.79 (t, 1F, F_{para}), −163.19 (m, 1F, F_{para}), −163.77 (m, 4F, F_{meta}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt). This compound was not stable enough in solution and decomposed during acquisition.

[Pt(CH₂C₆H₄-*o*-P(*o*-tol)₂)(PPh₃){C(CO₂Me)−C(PPh₃)(CO₂Me)}](ClO₄), 2. To a suspension of $[Pt(\mu\text{-}Cl)(CH_2C_6H_4\text{-}o\text{-}P(o\text{-tol})_2)]_2$ (0.160 g, 0.150 mmol) in dry THF (15 mL) was added $AgClO_4$ (0.063 g, 0.30 mmol), and the resulting mixture was stirred for 20 min at room temperature with exclusion of light. The insoluble AgCl was filtered off, and the solution of the solvato derivative was reacted with the bis-ylide (0.200 g, 0.300 mmol). The initial deep yellow suspension evolved to a colorless solution, and some decomposition was evident (presence of Pt^0). After the reaction time (3 h) any insoluble impurity was removed by filtration and the resulting solution was evaporated to dryness. Treatment of the residue with Et_2O (15 mL) gave **2** as a pale yellow solid, which was filtered, washed with Et_2O (15 mL), and air-dried. Obtained: 0.248 g (65% yield).

Anal. Calcd for $[C_{63}H_{56}ClO_8P_3Pt]$: C, 59.83; H, 4.56. Found: C, 59.47; H, 4.53. MS (FAB+) [*m/z*, (%)]: 1165 (10%) $[(M - ClO_4)^+]$, 902 (100%) $[(M - ClO_4 - PPh_3)^+]$. IR (ν, cm^{-1}): 1710, 1691 ($\nu_{C=O}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.77−6.89 (m, 40H, Ph + Tol), 6.63 (t, 1H, C_6H_4, $^3J_{H-H}$ = 8.0 Hz), 6.29 (dd, 1H, $^3J_{H-H}$ = 10.0 Hz, $^3J_{H-H}$ = 8.0 Hz), 3.60, 3.48 (AB part of an ABX spin system (X = ^{31}P), 2H, CH_2Pt, $^2J_{HH'}$ = 16.8 Hz,$^3J_{HP}$ = 6.9 Hz,$^3J_{H'P}$ = 8.4 Hz), 3.26 (s, 3H, OMe), 2.57 (s, 3H, OMe), 2.48 (s, 3H, Me), 1.87 (s, 3H, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 28.25 (dd, 1P, P(*o*-tol)₂, $^4J_{PP}$ = 35.3 Hz, $^2J_{PPcis}$ = 14.8 Hz, $^1J_{PtP}$ = 2519 Hz), 18.95 (dd, 1P, Pt−PPh_3, $^4J_{PP}$ = 5.6 Hz, $^2J_{PPcis}$ = 14.8 Hz, $^1J_{PtP}$ = 2056 Hz), 15.57 (dd, 1P, −C(PPh_3), $^4J_{PP}$ = 35.3 Hz, $^4J_{PP}$ = 5.6 Hz, $^3J_{PPt}$ = 305 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 217.21 (dd, Pt=C, $^2J_{Ptrans-C}$ = 109 Hz, $^2J_{P-C}$ = 8.5 Hz), 171.37 (d, CO_2, $^3J_{PC}$ = 14.4 Hz), 167.65 (d, CO_2, $^2J_{PC}$ = 23.1 Hz), 155.89 (dd, C_6H_4, J_{PC} = 33.8 Hz, J_{PC} = 2.4 Hz), 142.21 (dd, C_6H_4, J_{PC} = 34.3 Hz, J_{PC} = 11.6 Hz), 138.24 (dd, C_6H_4, J_{PC} = 60.3 Hz, J_{PC} = 10.7 Hz), 135.18−125.19 (m, Ph + C_6H_4), 120.49 (d, C_{ipso}, Ph, $^1J_{PC}$ = 88.3 Hz), 110.77 (dd, =C(P), $^1J_{PC}$ = 70.9 Hz, $^3J_{PC}$ = 2.7 Hz), 52.49 (s, OMe), 51.14 (s, OMe), 37.09 (d, CH_2Pt, $^2J_{Ptrans-C}$ = 87.1 Hz, $^1J_{Pt-C}$ = 548 Hz), 23.53 (d, Me, $^3J_{PC}$ = 9.1 Hz), 22.78 (d, Me, $^3J_{PC}$ = 6.4 Hz).

[Pd(CH₂C₆H₄-*o*-P(*o*-tol)₂)(PPh₃){C(CO₂Me)−C(PPh₃)(CO₂Me)}](ClO₄), 3. Complex **3** was prepared following an experimental method similar to that described for **2**. $[Pd(\mu\text{-}Cl)(CH_2C_6H_4\text{-}o\text{-}P(o\text{-tol})_2)]_2$ (0.100 g, 0.113 mmol) was reacted with $AgClO_4$ (0.047 g, 0.23 mmol) and with the bis-ylide (0.150 gr, 0.225 mmol) in dry THF to give **3** as a yellow solid. Obtained: 0.264 g, (96% yield). Complex **3** was recrystallized from CH_2Cl_2/Et_2O to give yellow crystals of **3**·0.25CH₂Cl₂. The amount of CH_2Cl_2 in the crystals was assayed by integration of the corresponding resonance in the ^1H NMR.

Anal. Calcd for $[C_{63}H_{56}ClO_8P_3Pd]\cdot 0.25CH_2Cl_2$: C, 63.46; H, 4.75. Found: C, 63.28; H, 4.99. MS (FAB+) [*m/z*, (%)]: 1075 (25%) $[(M - ClO_4)^+]$, 813 (100%) $[(M - ClO_4 - PPh_3)^+]$. IR (ν, cm^{-1}): 1724, 1708 ($\nu_{C=O}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.67−6.98 (m, 40H, Ph + Tol), 6.87 (t, 1H, C_6H_4, $^3J_{HH}$ = 8.4 Hz), 6.54 (t, 1H, C_6H_4, $^3J_{HH}$ = 8.4 Hz), 3.95, 3.61 (AB part of an ABX spin system (X = ^{31}P), 2H, CH_2Pd, $^2J_{HH}$ = 16.5 Hz), 2.50 (s, 3H, OMe), 2.47 (s, 3H, OMe), 1.95 (s, 3H, Me(tol)), 1.62 (s, 3H, Me(tol)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 28.93 (s, br, P(tol)₂), 21.70 (s, br, Pd−PPh_3), 11.55 (s, −C(PPh_3)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 170.49 (s, CO_2), 169.51 (dd, CO_2, J_{PC} = 10.0 Hz, J_{PC} = 3.6 Hz), 148.74 (d, C_6H_4, J_{PC} = 22.7 Hz), 142.13 (d, C_6H_4, J_{PC} = 15.8 Hz), 141.79 (d, C_6H_4, J_{PC} = 13.9 Hz), 136.67−126.56 (m, Ph + C_6H_4), 123.85 (d, C_{ipso}, Ph, $^1J_{PC}$ = 89.6 Hz), 52.43 (s, OMe), 51.43 (s, OMe), 41.29 (s, CH_2Pd), 23.58 (d, Me, $^3J_{PC}$ = 13.1 Hz), 22.52 (d, Me, $^3J_{PC}$ = 12.9 Hz). The carbenic carbon Pd=C_α (220−200 ppm) and the ylidic C_β carbon (about 110 ppm) were not observed despite long accumulation trials.

[Pd(CH₂C₉H₆N-C⁸,N)(PPh₃){C(CO₂Me)−C(PPh₃)(CO₂Me)}](ClO₄), 4. Complex **4** was prepared following an experimental method similar to that described for **2**, except that complex **4** precipitated in THF. $[Pd(\mu\text{-}Cl)(CH_2C_9H_6N\text{-}C^8,N)]_2$ (0.063 g, 0.113 mmol) was reacted with $AgClO_4$ (0.047 g, 0.23 mmol) and with the bis-ylide (0.150 g, 0.225 mmol) in dry THF to give **4** as a yellow solid insoluble in THF. Obtained: 0.193 g (90% yield). Complex **4** was recrystallized from CH_2Cl_2/Et_2O to give yellow crystals of **4**·0.65CH₂Cl₂. The amount of CH_2Cl_2 in the crystals was estimated by integration of the corresponding resonance in the ^1H NMR.

Anal. Calcd for $[C_{52}H_{44}ClNO_8P_2Pd]\cdot 0.65CH_2Cl_2$: C, 59.10; H, 4.26; N, 1.31. Found: C, 58.95; H, 4.28; N, 1.40. MS (FAB+) [*m/z*, (%)]: 914 (70%) $[(M - ClO_4)^+]$, 652 (100%) $[(M - ClO_4 - PPh_3)^+]$. IR (ν, cm^{-1}): 1722, 1699 ($\nu_{C=O}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 8.53 (dd, 1H, 8mq, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.8 Hz), 8.29 (dd, 1H, 8mq, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.8 Hz), 7.87−7.29 (m, 33H, Ph + 8mq), 7.00 (dd, 1H, 8mq, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 5.1 Hz), 4.36 (d, 1H, $PdCH_2$, $^2J_{HH}$ = 16.5 Hz), 3.54 (ddd, 1H, $PdCH_2$, $^2J_{HH}$ = 16.5 Hz, $^3J_{PH}$ = 10.8 Hz, $^5J_{PH}$ = 1.5 Hz), 2.96 (s, 3H, OMe), 2.96 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 27.32 (s), 26.49 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 171.05 (pseudot, CO_2, J_{PC} = 4.8 Hz), 169.55 (d, CO_2, J_{PC} = 11.8 Hz), 157.31 (d, J_{PC} = 5 Hz), 144.38, 140.42, 139.06, 133.78, 130.77, 130.46, 127.66, 121.48 (C_9H_6N), 135.05 (d, C_{meta}, Ph, $^3J_{PC}$ = 10 Hz), 134.43 (d, C_{meta}, Ph, $^3J_{PC}$ = 14 Hz), 134.33 (s, C_{para}, Ph), 129.38−128.94 (m, $C_{ortho} + C_{para}$, Ph), 123.35 (d, C_{ipso}, Ph, $^1J_{PC}$ = 90.6 Hz), 52.73 (s, OMe), 51.58 (s, OMe), 38.55 (t, CH_2Pd, J_{PC} = 5.1 Hz). The carbenic carbon Pd=C_α (220−200 ppm) and the ylidic C_β carbon (about 110 ppm) were not observed despite long accumulation trials.

[Pd(NC₅H₄-*o*-C₆H₄)(PPh₃){C(CO₂Me)−C(PPh₃)(CO₂Me)}](ClO₄), 5. Complex **5** was prepared following an experimental method similar to that described for **2**, except that complex **5** precipitated in THF. $[Pd(\mu\text{-}Cl)(NC_5H_4\text{-}o\text{-}C_6H_4)]_2$ (0.066 g, 0.113 mmol) was reacted with $AgClO_4$ (0.047 g, 0.23 mmol) and with the bis-ylide (0.150 g, 0.225 mmol) in dry THF to give **5** as a white solid insoluble in THF. Obtained: 0.157 g (72% yield). Complex **5** was recrystallized from CH_2Cl_2/Et_2O to give colorless crystals of **5**·0.5CH₂Cl₂. The amount of CH_2Cl_2 in the crystals was determined by integration of the corresponding resonance in the ^1H NMR.

Anal. Calcd for $[C_{53}H_{44}ClNO_8P_2Pd]\cdot 0.5CH_2Cl_2$: C, 60.10; H, 4.24; N, 1.31. Found: C, 60.19; H, 4.22; N, 1.46. MS (FAB+) [*m*/*z*, (%)]: 664 (100%) $[(M - ClO_4 - PPh_3)^+]$. IR (ν, cm^{-1}): 1693 ($\nu_{C=O}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.90−7.38 (m, 34H, Ph + C_6H_4 + NC_5H_4), 7.10 (td, 1H, Ph-py, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz), 6.96 (t, 1H, Ph-py, $^3J_{HH}$ = 7.2 Hz), 6.75 (t, 1H, Ph-py, $^3J_{HH}$ = 7.2 Hz), 6.51 (td, 1H, Ph-py, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 0.9 Hz), 3.42 (s, 3H, OMe), 2.80 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 22.34 (d, Pd−PPh_3, $^4J_{PP}$ = 6.7 Hz), 14.78 (d, −C(PPh_3)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 220.69 (dd, Pd=C, $^2J_{PC}$ = 14.1 Hz, $^2J_{PC}$ = 10.2 Hz), 170.49 (d, CO_2, $^3J_{PC}$ = 13.5 Hz), 167.98 (d, CO_2, $^2J_{PC}$ = 23.7 Hz), 163.06, 161.66, 152.10 (d, J_{PC} = 6.2 Hz), 146.68, 139.48, 134.99, 129.75 (d, J_{PC} = 6.6 Hz), 125.83, 124.37 (d, J_{PC} = 4.6 Hz), 122.29, 119.65 ($C_{11}H_8N$), 135.75 (d, C_{meta}, Ph, $^3J_{PC}$ = 12.8 Hz), 134.43 (s, C_{para}, Ph), 134.04 (d, C_{meta}, Ph, $^3J_{PC}$ = 10.3 Hz), 131.54 (s, C_{para}, Ph), 130.05 (d, C_{ortho}, Ph, $^2J_{PC}$ = 12.9 Hz), 129.18 (d, C_{ortho}, Ph, $^2J_{PC}$ = 10.1 Hz), 120.72 (d, C_{ipso}, Ph, $^1J_{PC}$ = 88.6 Hz), 110.06 (d, =C(P), $^1J_{PC}$ = 77.4 Hz), 52.91 (s, OMe), 51.33 (s, OMe).

[Pd($C_{13}H_8N$)(PPh_3){C(CO_2Me)−C(PPh_3)(CO_2Me)}]-(ClO_4), 6. Complex **6** was prepared following an experimental method similar to that described for **2**, except that complex **6** precipitated in THF. [Pd(μ-Cl)($C_{13}H_8N$)]$_2$ (0.072 g, 0.113 mmol) was reacted with $AgClO_4$ (0.047 g, 0.23 mmol) and with the bis-ylide (0.150 gr, 0.225 mmol) in dry THF to give **6** as a white solid insoluble in THF. Obtained: 0.090 g (38% yield).

Anal. Calcd for $[C_{55}H_{44}ClNO_8P_2Pd]$: C, 62.87; H, 4.22; N, 1.33. Found: C, 62.56; H, 4.13; N, 1.50. MS (FAB+) [*m*/*z*, (%)]: 950 (10%) $[(M - ClO_4)^+]$, 688 (100%) $[(M - ClO_4 - PPh_3)^+]$. IR (ν, cm^{-1}): 1695 ($\nu_{C=O}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 8.20 (dd, 1H, $C_{13}H_8N$, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz), 7.96−7.91 (m, 6H, Ph), 7.81−7.73 (m, 4H, $C_{13}H_8N$), 7.63−7.55 (m, 9H, Ph), 7.53−7.44 (m, 15H, Ph), 7.15 (m, 2H, $C_{13}H_8N$), 6.91 (dd, 1H, $C_{13}H_8N$, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 5.4 Hz), 3.38 (s, 3H, OMe), 2.80 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 22.18 (d, Pd−PPh_3,$^4J_{PP}$ = 6.10 Hz), 14.68 (d, −C(PPh_3)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 219.67 (dd, Pd=C, $^2J_{PC}$ = 13.1 Hz, $^2J_{PC}$ = 9.9 Hz), 170.49 (d, CO_2, $^3J_{PC}$ = 13.1 Hz), 168.06 (dd, CO_2, $^2J_{PC}$ = 21.0 Hz, $^4J_{PC}$ = 1.9 Hz), 161.61, 160.18, 156.02 (d, J_{PC} = 5.2 Hz), 151.14 (d, J_{PC} = 4.8 Hz), 142.15, 138.45, 132.61, 129.90, 128.98 (d, J_{PC} = 7.2 Hz), 127.71, 124.36, 123.99, 121.51 ($C_{13}H_8N$), 135.81 (d, C_{meta}, Ph, $^3J_{PC}$ = 12.8 Hz), 134.49 (d, C_{para}, Ph, $^4J_{PC}$ = 2.6 Hz), 134.03 (d, C_{meta}, Ph, $^3J_{PC}$ = 10.3 Hz), 131.58 (s, C_{para}, Ph), 130.11 (d, C_{ortho}, Ph, $^2J_{PC}$ = 12.9 Hz), 129.21 (d, C_{ortho}, Ph, $^2J_{PC}$ = 9.8 Hz), 120.79 (d, C_{ipso}, Ph, $^1J_{PC}$ = 88.7 Hz), 110.14 (dd, =C(P), $^1J_{PC}$ = 71.2 Hz, $^3J_{PC}$ = 3.8 Hz), 52.95 (s, OMe), 51.38 (s, OMe).

Reaction of [Pt(Cl)($CH_2C_6H_4$-*o*-P(*o*-tol)$_2$)(PPh_3)] with the Bis-ylide Ph_3P=C(CO_2Me)−C(CO_2Me)=PPh_3. To a solution of [Pt(Cl)($CH_2C_6H_4$-*o*-P(*o*-tol)$_2$)(PPh_3)] (0.178 g, 0.225 mmol) in dry THF (20 mL) was added $AgClO_4$ (0.047 g, 0.23 mmol), and the resulting mixture was stirred for 20 min at room temperature with exclusion of light. The AgCl that precipitated was filtered off, and the resulting solution of the solvato derivative was treated with the bis-ylide (0.150 g, 0.225 mmol). The initial yellow suspension gradually dissolved (about 30 min). This solution was evaporated to small volume (≈5 mL), and by Et_2O (20 mL) addition the complex [Pt($CH_2C_6H_4$-*o*-P(*o*-tol)$_2$)(PPh_3)$_2$](ClO_4), **7**, was obtained as a yellow solid. Obtained: 0.235 g (93% yield). The evaporation of the ether solution gave a solid residue, which was identified as a mixture of dimethylfumarate and O=PPh_3 by ^1H and $^{31}P\{^1H\}$ NMR analysis.

Anal. Calcd for $[C_{57}H_{50}ClO_4P_3Pt]$: C, 60.99; H, 4.49. Found: C, 60.78; H, 4.44. MS (FAB+) [*m*/*z*, (%)]: 1022 (15%) $[(M - ClO_4)^+]$, 760 (100%) $[(M - PPh_3 - ClO_4)^+]$. ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.47−6.88 (m, 41H, C_6H_4 + Tol + Ph), 6.62 (dd, 1H, C_6H_4, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.4 Hz), 3.23 (s, br, 2H, $PtCH_2$, $^2J_{PtH}$ = 63 Hz), 2.29 (s, 6H, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 43.05 (dd, PPh_3 *trans* P(tol)$_2$, $^2J_{PPtrans}$ = 364.5 Hz, $^2J_{PPcis}$ = 21.86 Hz, $^1J_{PtP}$ = 1509 Hz), 28.20 (dd, P(tol)$_2$, $^2J_{PPcis}$ = 20.65 Hz, $^1J_{PtP}$ = 1392 Hz), 18.78 (dd, PPh_3 *cis* P(tol)$_2$, $^1J_{PtP}$ = 989 Hz).

Reaction of [Pd(Cl)($CH_2C_9H_6N$-C^8,N)(PPh_3)] with the Bis-ylide Ph_3P=C(CO_2Me)−C(CO_2Me)=PPh_3. In a way similar to that described in the preceding paragraphs, [Pd(Cl)-($CH_2C_9H_6N$-C^8,N)(PPh_3)] (0.123 g, 0.225 mmol) reacted with $AgClO_4$ (0.047 g, 0.23 mmol) and with the bis-ylide (0.150 g., 0.225 mmol) in dry THF (20 mL) to give [Pd($CH_2C_9H_6N$-C^8,N)-(PPh_3)$_2$](ClO_4), **8**, as a pale yellow solid. Obtained: 0.128 g (65.2% yield). The evaporation of the ether solution gave a solid residue, which was identified as a mixture of dimethylfumarate and O=PPh_3 by ^1H and $^{31}P\{^1H\}$ NMR analysis.

Anal. Calcd for $[C_{46}H_{38}ClNO_4P_2Pd]$: C, 63.31; H, 4.39; N, 1.60. Found: C, 62.63; H, 4.34; N, 1.56. MS (FAB+) [*m*/*z*, (%)]: 772 (5%) $[(M - ClO_4)^+]$, 510 (100%) $[(M - ClO_4 - PPh_3)^+]$. ^1H NMR (CD_2Cl_2 rt): δ (ppm), 8.27 (dd, 1H, C_9H_6N, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz), 7.93 (s, br, 1H, C_9H_6N), 7.70 (d, 1H, C_9H_6N, $^3J_{HH}$ = 7.80 Hz), 7.66−7.16 (m, 32H, Ph + C_9H_6N), 6.87 (dd, 1H, C_9H_6N, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 5.7 Hz), 3.27 (s, 2H, $PdCH_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 38.58 (d,$^2J_{PP}$ = 37.7 Hz), 20.87 (d).

[Pd{*trans*-*C*(C_6F_5)(CO_2Me)−*C*(PPh_3)(CO_2Me)}(tht)-(PPh_3)](ClO_4), 9. To a solution of [Pd(μ-Cl)(C_6F_5)(SC_4H_8)]$_2$ (0.089 g, 0.113 mmol) in dry THF (20 mL) was added $AgClO_4$ (0.047 g, 0.23 mmol). The resulting mixture was stirred for 20 min with exclusion of light and then filtered to remove the AgCl that precipitated. To the freshly prepared solution of the solvato derivative the bis-ylide (0.150 g, 0.225 mmol) was added, resulting in the immediate formation of a yellow solution. This solution was evaporated to one-third of the initial volume and stirred for 3 h at room temperature. After this time a yellow precipitate appeared, which was filtered, washed with THF (2 mL) and Et_2O (15 mL), air-dried, and identified as **9**. Obtained: 0.115 g (45.5% yield). The THF solution was further evaporated, giving a second crop of **9**. Obtained: 0.046 g (18.2% yield). Total obtained: 0.161 g (63.7% net yield). The spectroscopic characterization of **9** revealed the presence of two isomers (**9a** and **9b**) in a **9a**:**9b** = 5:1 molar ratio.

Anal. Calcd for $[C_{52}H_{44}ClF_5O_8P_2PdS]$: C, 55.38; H, 3.93; S, 2.84. Found: C, 55.01; H, 3.99; N, 2.99. MS (FAB+) [*m*/*z*, (%)]: 939 (10%) $[(M - ClO_4 - SC_4H_8)^+]$, 677 (40%) $[(M - ClO_4 - SC_4H_8 - PPh_3)^+]$, 571 (100%) $[(M - Pd - ClO_4 - SC_4H_8 - PPh_3)^+ \equiv (C_6F_5C(CO_2Me)C(CO_2Me)PPh_3)^+]$. IR ($\nu$, cm^{-1}): 1695 ($\nu_{C=O}$), 1244 (SC_4H_8), 982, 922 (C_6F_5). ^1H NMR ($CDCl_3$, rt): δ (ppm), 7.68−7.33 (m, Ph), 3.44 (s, OMe, **9b**), 2.89 (s, OMe, **9a**), 2.83 (s, OMe, **9a**), 2.80 (s, OMe, **9b**), 2.64 (m, SC_4H_8, both), 2.43 (m, SC_4H_8, both), 1.57 (s, SC_4H_8, both). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 29.08 (d, P_A, **9b**,$^3J_{PP}$ = 18.2 Hz), 28.56 (s, P_A, **9a**), 25.92 (d, P_B, **9a**, $^5J_{PF}$ = 26 Hz), 23.18 (d, P_B, **9b**). ^{19}F NMR (CD_2Cl_2, ta): δ (ppm), −131.35 (d, F_o, **9b**, J_{FF} = 22.6 Hz), −134.04 (d, F_o, **9a**, J_{FF} = 22.6 Hz), −134.25 (t, F_o, **9a**, $J_{FF} \approx J_{PF}$ = 26 Hz), −136.29 (d, F_o, **9b**, J_{FF} = 25 Hz), −152.97 (t, F_p, **9b**, J_{FF} = 22.6 Hz), −154.84 (t, F_p, **9a**, J_{FF} = 22.6 Hz), −161.32 (t, F_m, **9b**), −161.83 (t, F_m, **9a**), −162.57 (t, F_m, **9b**), −162.77 (t, F_m, **9a**).

[Pd{*trans*-*C*(C_6F_5)(CO_2Me)−*C*(PPh_3)(CO_2Me)}(PPh_3)$_2$]-(ClO_4), 10. Complex **10** was prepared following the same experimental method as that described for **9**, except that the product was precipitated with Et_2O after evaporation to dryness of the THF solution. [Pd(μ-Cl)(C_6F_5)(PPh_3)]$_2$ (0.128 g, 0.113 mmol) was reacted in dry THF (10 mL) with $AgClO_4$ (0.047 g, 0.23 mmol) and the bis-ylide (0.150 g, 0.225 mmol) to give **10** as a pale orange solid. Obtained: 0.158 g (53.9% yield).

Anal. Calcd for $[C_{66}H_{51}ClF_5O_8P_3Pd]$: C, 60.89; H, 3.95. Found: C, 60.54; H, 3.91. IR (ν, cm^{-1}): 1698, 1677 ($\nu_{C=O}$), 985, 914 (C_6F_5). MS (FAB+) [*m*/*z*, (%)]: 939 (10%) $[(M - ClO_4 - PPh_3)^+]$, 677 (25%) $[(M - ClO_4 - 2PPh_3)^+]$, 571 (100%) $[(M - Pd - ClO_4 - 2PPh_3)^+ \equiv (C_6F_5C(CO_2Me)C(CO_2Me)PPh_3)^+]$. ^1H

NMR ($CDCl_3$, rt): δ (ppm), 7.79−7.09 (m, 45H, Ph), 2.73 (s, 3H, OMe), 2.65 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 29.97 (d, P_A,$^3J_{PAPB} = 17.5$ Hz), 23.22 (dd, P_B, $^2J_{PBPC} = 26.0$ Hz), 21.44 (t, P_C, $^5J_{PCF} \approx {}^2J_{PBPC} = 26$ Hz). ^{19}F NMR (CD_2Cl_2, rt): δ (ppm), −129.99 (d, F_o, $J_{FF} = 17$ Hz), −131.30 (t, F_o, $J_{FF} \approx J_{PF} = 26$ Hz), −155.95 (t, F_p, $J_{FF} = 19$ Hz), −161.35 (t, F_m), −163.37 (t, F_m).

Reactivity of the Mixture 9a/9b. NMR Experiments. (a) To a solution of **9** (25 mg, 0.022 mmol) in $CDCl_3$ (0.4 mL) was added PPh_3 (6 mg, 0.02 mmol). The initial yellow color of **9** changed in a few seconds to pale orange. The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were registered 5 min after mixture (time for locking and shimming). The NMR spectra showed the presence of a mixture **9**/PPh_3/**10** in a 0.25:0.5:1 molar ratio. (b) To a solution of **9** (25 mg, 0.022 mmol) in CD_2Cl_2 (0.4 mL) was added bis(diphenylphosphino)methane (dppm, 9 mg, 0.02 mmol). The yellow color of **9** dissappeared instantaneously, giving a colorless solution. The NMR spectra of this solution showed, exclusively, signals corresponding to **11a**. (c) To a solution of **9** (25 mg, 0.022 mmol) in CD_2Cl_2 (0.4 mL) was added bis(diphenylphosphino)ethane (dppe, 9 mg, 0.02 mmol). A colorless solution was obtained in a few seconds. The NMR spectra of this solution showed, exclusively, signals corresponding to **11b**.

Spectroscopic Characterization of 11a. ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.81−6.63 (m, Ph), 4.20 (m, 1H, PCH_2P), 3.34 (m, 1H, PCH_2P), 2.82 (s, 3H, OMe), 2.50 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 26.97 (d, P_A,$^3J_{PAPC} = 16.4$ Hz), 24.27 (t, P_B, $^5J_{PBF} \approx {}^2J_{PBPC} = 26$ Hz), 17.91 (m, P_C), −21.70 (d, P_D, $^2J_{PDPC} = 23.1$ Hz). ^{19}F NMR (CD_2Cl_2, ta): δ (ppm), −131.19 (s, br, F_o), −132.32 (t, F_o, $J_{FF} \approx J_{PF} = 26$ Hz), −156.61 (t, F_p, $J_{FF} = 23$ Hz), −161.33 (t, F_m), −164.04 (t, F_m).

Spectroscopic Characterization of 11b. ^1H NMR (CD_2Cl_2, rt): δ (ppm), 8.01−6.44 (m, Ph), 2.64 (s, 3H, OMe), 2.46 (s, 3H, OMe) 2.12−1.80 (m, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 27.48 (d, P_A,$^3J_{PAPC} = 16.1$ Hz), 23.75 (t, P_B, $^5J_{PBF} \approx {}^2J_{PBPC} = 30$ Hz), 19.77 (td, P_C), −14.86 (d, P_D, $^3J_{PDPC} = 30.3$ Hz). ^{19}F NMR (CD_2Cl_2, ta): δ (ppm), −131.16 (s, br, F_o), −132.29 (t, F_o, $J_{FF} \approx J_{PF} = 30$ Hz), −156.65 (t, F_p, $J_{FF} = 23$ Hz), −161.44 (t, F_m), −164.07 (t, F_m).

Reactivity of $Hg(OAc)_2$ with the Bis-ylide. To a suspension of $Hg(OAc)_2$ (0.072 g, 0.23 mmol) in dry THF (20 mL) was added the bis-ylide (0.150 g, 0.225 mmol). The resulting suspension was stirred at room temperature for 24 h. The initial yellow suspension changed gradually to gray, and, after the reaction period, the suspension was filtered. The resulting gray solid was recrystallized from CH_2Cl_2/Et_2O, giving a white solid, characterized as $[Hg(OAc)_2(PPh_3)]$, **12**. Obtained: 0.052 g, (40% yield based on Hg). The yellowish THF solution was evaporated to dryness and the oily residue treated with Et_2O (10 mL), giving a yellow solid (0.120 g) characterized by NMR as a mixture of the starting compounds. The ether solution was allowed to stand for 24 h at room temperature. During this time, colorless crystals of the ylide **13** were formed, which were collected and air-dried. Obtained: 0.043 g, (45% yield based on bis-ylide).

Characterization of **12**. Anal. Calcd for $[C_{22}H_{21}HgO_4P]$: C, 45.48; H, 3.64. Found: C, 45.34; H, 3.55. MS (FAB+) [*m*/*z*, (%)]: 522 (100%) $[(M - OAc)^+]$. IR (ν, cm^{-1}): 1582 (ν_{CO}, OAc), 530, 505, 495 (PPh_3). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.68−7.54 (m, 15 H, Ph), 1.83 (s, 6H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 32.65 (s, $^1J_{HgP} = 8389$ Hz).

Characterization of **13**. Anal. Calcd for $[C_{24}H_{21}O_5P]$: C, 68.57; H, 5.03. Found: C, 68.31; H, 4.90. MS (FAB+) [*m*/*z*, (%)]: 421 (10%) $[(M + H)^+]$, 361 (100%) $[(M - CO_2Me)^+]$. IR (ν, cm^{-1}): 1740 (ν_{CO}), 1671 (ν_{COOMe}), 1564 ($\nu_{P=C-COOMe}$). ^1H NMR (CD_2Cl_2, rt): δ (ppm), 7.69−7.57 (m, 6H, Ph), 7.56−7.54 (m, 3H, Ph), 7.50−7.44 (m, 6H, Ph), 3.83 (s, 3H, OMe), 3.27 (s, 3H, OMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 16.60. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, rt): δ (ppm), 184.38 (d, CO, $^2J_{PC} = 6.2$ Hz), 167.79 (d, CO_2, $J_{PC} = 14.8$ Hz), 167.55 (d, CO_2, $J_{PC} = 13.2$ Hz), 133.64 (d, C_{meta}, Ph, $^3J_{PC} = 10.2$ Hz), 132.54 (d, C_{para}, Ph, $^4J_{PC} = 2.7$ Hz), 128.79 (d, C_{ortho}, Ph, $^2J_{PC} = 12.8$ Hz), 123.92 (d, C_{ipso}, Ph, $^1J_{PC} = 93.3$ Hz), 68.04 (d, P=C, $^1J_{PC} = 111.2$ Hz), 51.89 (s, OMe), 50.34 (s, OMe).

Crystal Structure Determination of Complex 1a·CH_2Cl_2. Crystals of complex **1a**·CH_2Cl_2 of adequate quality for X-ray measurements were grown by slow vapor condensation of Et_2O over a CH_2Cl_2 solution of crude **1a** at room temperature. A single crystal of dimensions 0.23 × 0.11 × 0.10 mm was mounted at the end of a quartz fiber in a random orientation and covered with epoxy.

Data Collection. Data collection was performed at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was collected based on three ω-scan runs (starting $\omega = -30°$) at values $\phi = 0°$, 90°, and 180° with the detector at $2\theta = 30°$. For each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 30 s per frame. The diffraction frames were integrated using the program SAINT,[33] and the integrated intensities were corrected for absorption with SADABS.[34]

Structure Solution and Refinement. The structure was solved and developed by Patterson and Fourier methods.[35] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The two interstitial dichloromethane molecules are disordered, each in two equally populated congeners. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[36] Crystallographic calculations were done on an AlphaStation (OPEN/VMS V6.2).

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Supporting Information Available: A drawing of complex **1a**·CH_2Cl_2. Tables giving complete data collection parameters, atomic coordinates, complete bond distances and angles, and thermal parameters for **1a**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) *SAINT* Version 5.0; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(34) Sheldrick, G. M. *SADABS*: Empirical absorption correction program; Göttingen University, 1996.

(35) Sheldrick, G. M. *SHELXS-86*, *Acta Crystallogr.* **1990**, *A46*, 467.

(36) Sheldrick, G. M. *SHELXL-97*: FORTRAN program for the refinement of crystal structures from diffraction data; Göttingen University, 1997. Molecular graphics were done using the commercial package *SHELXTL-PLUS*, Release 5.05/V; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.