the acrylamide ligand in these systems is an excellent illustration of the potential usefulness of binuclear complexes in organic synthesis.

Acknowledgment. We gratefully acknowledge support of this work by grants (R.S.D., A.H.W.) from the Australian Research Grants Scheme.

Registry No. 1, 98395-25-6; **2a**, 90860-67-6; **2b**, 90883-06-0; **2c**, 90860-68-7; **2d**, 98395-26-7; **2e**, 90860-73-4; **2f**, 90860-72-3; **2g**, 90860-65-4; **2h**, 90860-66-5; **2i**, 90883-05-9; **3** (R = Cy), 98464-04-1; **3** (R = *i*-Pr), 98464-05-2; **3** (R = *t*-Bu), 71853-17-3; (η-C_5H_5)-$Rh_2(CO)_2(CF_3C_2CF_3)$, 57872-13-6; (η-C_5H_5)$_3$$Rh_3(CO)(CF_3C_2CF_3)$, 37343-45-6; *cis*-$(MeO_2C)CH{=}C(CO_2Me)N_3$, 36875-40-8; *trans*-$(MeO_2C)CH{=}C(CO_2Me)N_3$, 36875-41-9; phenyl azide, 622-37-7; benzoyl azide, 582-61-6; *p*-toluenesulfonyl azide, 941-55-9; *N*,*N*′-dicyclohexylcarbodiimide, 538-75-0; *N*,*N*′-diisopropylcarbodiimide, 693-13-0; methyl isocyanate, 624-83-9; *tert*-butyl isocyanate, 1609-86-5; *p*-tolyl isocyanate, 622-58-2.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters, hydrogen atom parameters, ring planes, and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

A Kinetic Study of the Generation of Terminal Phosphinidene Complexes from 7-Phosphanorbornadiene Complexes. X-ray Crystal Structure Analysis of the Dimers of Terminal Phosphinidene Complexes

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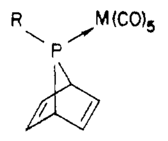
A kinetic study of the thermal decomposition of a 7-phenyl-7-phosphanorbornadiene P—$W(CO)_5$ complex in the presence of aniline, tolan, and cyclooctene has been performed at 105, 115, 117, and 125 °C. The kinetics of this decomposition are first order in the concentration of the phosphanorbornadiene complex and do not depend on the concentration and nature of the trapping reagent. These results give additional support to the intermediacy of a terminal phosphinidene complex, [PhP=$W(CO)_5$], in such a decomposition. The activation energy of the process is calculated to be 33 ± 1 kcal mol^{-1}. The thermolysis of the same 7-phosphanorbornadiene at 55 °C in the presence of CuCl as a catalyst gives a dimeric complex, [PhP=PPh][$W(CO)_5$]$_3$, in which both the phosphorus atoms and the P=P double bond are complexed by the three $W(CO)_5$ units as shown by X-ray crystal structure analysis.

Recently, we have studied the thermal reactions of 7-phosphanorbornadiene complexes 1 with a variety of organic and inorganic reagents including primary and secondary amines,[2] alcohols,[2] water,[2] alkenes,[3] conjugated dienes,[3] enamines,[4] alkynes,[5] etc. In each case, the products of the reactions were best explained by assuming the intermediacy of a terminal phosphinidene complex, **2**, resulting from the collapse of the phosphorus bridge of the 7-phosphanorbornadiene skeleton. Since then, other authors have attempted to stabilize such terminal phosphinidene complexes but they have been unsuccessful as of yet.[6,7] Thus, the existence of terminal phosphinidene complexes so far relies only on a range of successful trapping reactions. In view of the theoretical importance of such species (they are the phosphorus analogues of carbene and nitrene complexes) and of their highly diversified suspected reactivity,[2-5] we thought that it would be interesting to provide additional evidence in favor of their (at least) transient existence. We thus decided to study the kinetics of the reactions of 7-phosphanorbornadiene complexes with a selection of efficient trapping reagents and to establish what were the products of the thermal decomposition of 7-phosphanorbornadienes when no trapping reagent was added to the reaction medium.



1

$R{-}P{=}M(CO)_5$

2

M=Cr, W

Results and Discussion

All our experiments were performed with the readily available tungsten complex **3**. We selected three representative trapping reagents, aniline, tolan, and cyclooctene. In the first two cases, the reaction with **3** is quantitative and no by-product is formed according to ^{31}P NMR studies. In the third case, the reaction was normally run in the presence of CuCl as a catalyst around 55 °C. Thus, in order to get comparable data, it was first necessary to check whether or not the same reaction could be run without catalyst at higher temperature. Since we suspected that previous failures were due to the thermal instability of phosphiranes, we decided to repeat our attempts with the most stable phosphiranes at the lowest possible temperatures. In so doing, we found that it was

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[1] (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.

[2] Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.

[3] Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

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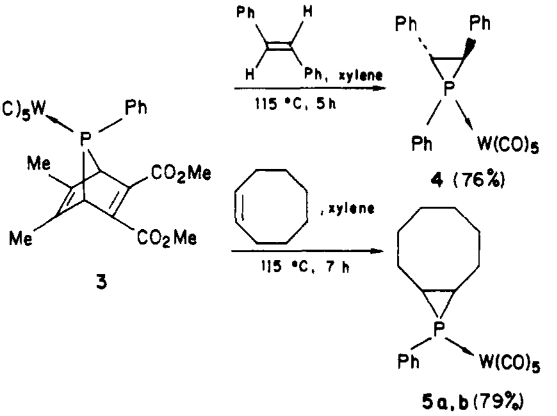
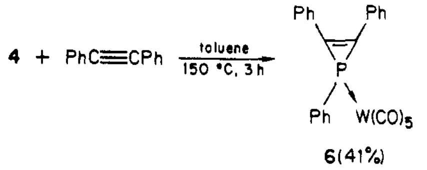
indeed possible to react both *trans*-stilbene and cyclooctene with **3** without CuCl to obtain the corresponding phosphiranes. The yields are given for the purified products after column chromatography. According to ^{31}P NMR no byproduct is formed. These successful experiments confirm that the role of the catalyst is to promote the decomposition of the 7-phosphanorbornadiene skeleton and not to interfere with the condensation of the suspected transient terminal phosphinidene complex with olefins. Our preceding failures at 150 °C also suggest that, somewhere between 115 and 150 °C, the phosphirane complexes decompose. Thus, it was interesting to check whether or not phosphirane complexes in turn could be used as generators of terminal phosphinidene complexes. This is indeed the case since the reaction of **4** with tolan at 150 °C gives the corresponding phosphirene complex.





The modest yield of **6** after purification by chromatography reflects the low scale of the experiment. In fact, according to the ^{31}P NMR spectroscopy, the reaction appears to be almost quantitative. This kind of experiment is related to the work of Quast, who has demonstrated that tris-tert-butylphosphirane oxide could be used as a thermal generator of *tert*-butylphosphinidene oxide.[8] Of course, as generators of terminal phosphinidene complexes, phosphirane complexes are far less useful than 7-phosphanorbornadiene complexes due to their higher decomposition temperatures.

The kinetic experiments were performed by using perdeuterioxylene as the solvent. The reactions were run at 105, 115, 117, and 125 °C. At these temperatures, the reactions are neither too fast nor too slow and can be appropriately followed by ^1H NMR spectroscopy. We have monitored the disappearance of the methoxy signals of **3** and the appearance of the methoxy signals of the phthalate **7**. The data are summarized on Figures 1–5. It is clear that the kinetics of the disappearance of **3** is independent of both the concentration and the nature of the trapping reagent and is first order in the concentration of **3**:$d[\mathbf{3}]/dt = -k[\mathbf{3}]$. These findings are obviously in agreement with the two-step mechanism shown in Scheme I.

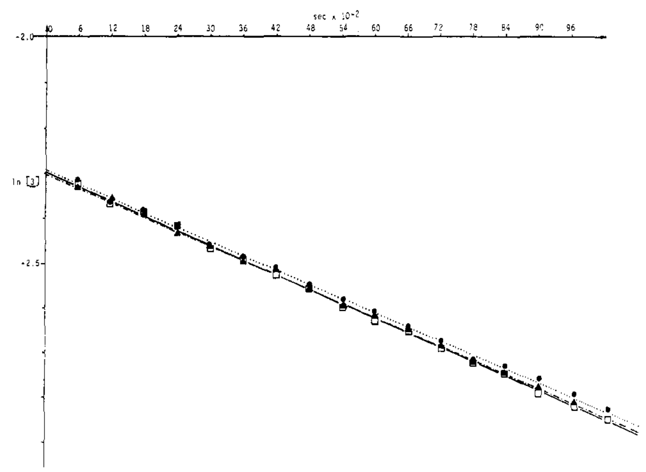


Figure 1. Kinetic data for the reactions of **3** with tolan, cyclooctene and aniline at 105 °C (± 1 °C) in perdeuterioxylene ($[\mathbf{3}]_{t_0}$ = 0.1019 mol × L^{-1}, time in s): □, $[\mathbf{3}]_{t_0}$:[PhC≡CPh] = 1:1, k = 5.45 × 10^{-5} s^{-1}, R = –0.9994; ▲, $[\mathbf{3}]_{t_0}$:[C_8H_{14}] = 1:2.3, k = 5.35 × 10^{-5} s^{-1}, R = –0.9985; ●, $[\mathbf{3}]_{t_0}$:[$PhNH_2$] = 1:5, k = 5.26 × 10^{-5} s^{-1}, R = –0.9976.

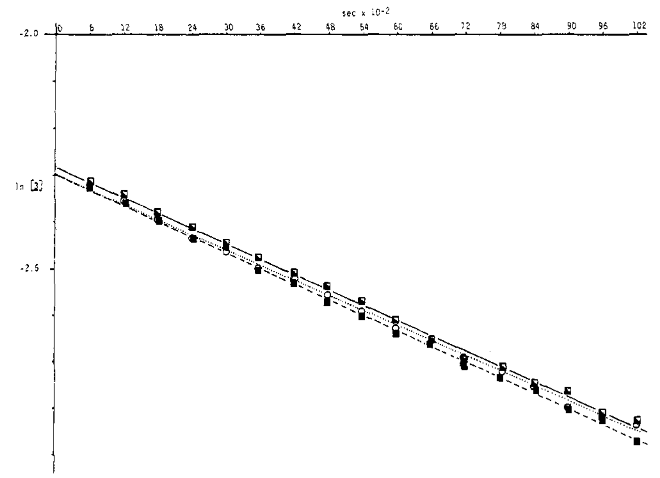


Figure 2. Kinetic data for the reactions of **3** with tolan and aniline at 105 °C (±1 °C) in perdeuterioxylene ($[\mathbf{3}]_{t_0}$ = 0.1019 mol × L^{-1}; time in s): ○, $[\mathbf{3}]_{t_0}$:[$PhNH_2$] = 1:1, k = 5.42 × 10^{-5} s^{-1}, R = –0.9971; ◩, $[\mathbf{3}]_{t_0}$:[PhC≡CPh] = 1:2.3, k = 5.45 × 10^{-5} s^{-1}, R = –0.9985; ■, $[\mathbf{3}]_{t_0}$:[PhC≡CPh] = 1:5, k = 5.58 × 10^{-5} s^{-1}, R = –0.9989.

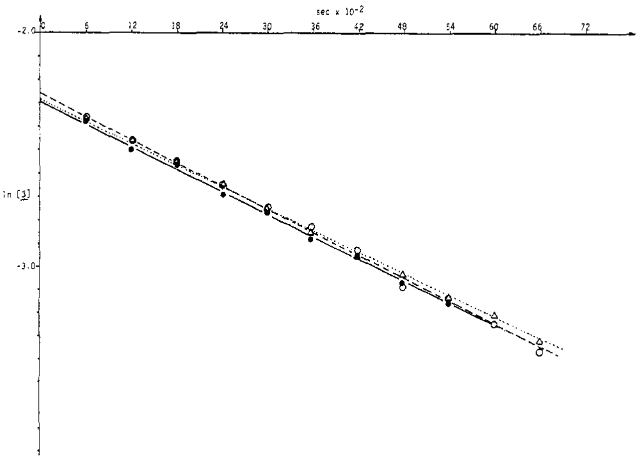


Figure 3. Kinetic data for the reactions of **3** with aniline and cyclooctene at 115 °C (±1 °C) in perdeuterioxylene ($[\mathbf{3}]_{t_0}$ = 0.1019 mol × L^{-1}; time in s): ○, $[\mathbf{3}]_{t_0}$:[$PhNH_2$] = 1:1, k = 1.67 × 10^{-4} s^{-1}, R = –0.9983; △, $[\mathbf{3}]_{t_0}$:[C_8H_{14}] = 1:1, k = 1.55 × 10^{-4} s^{-1}, R = –0.9992; ●, $[\mathbf{3}]_{t_0}$:[$PhNH_2$] = 1:5, k = 1.59 × 10^{-4} s^{-1}, R = –0.9957.

The first step involves the slow decomposition of **3** giving rise to the phthalate **7** and to the suspected terminal phosphinidene complex **8**, the existence of which is now more firmly established. Using the classical formulas and the data of Figures 1–5, the activation energy of this rate-determining step is calculated to be 33 ± 1 kcal mol^{-1}. The highly electrophilic complex **8** (according to theoretical

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(8) Quast, H.; Heuschmann, M. *Chem. Ber.* **1982**, *115*, 901.

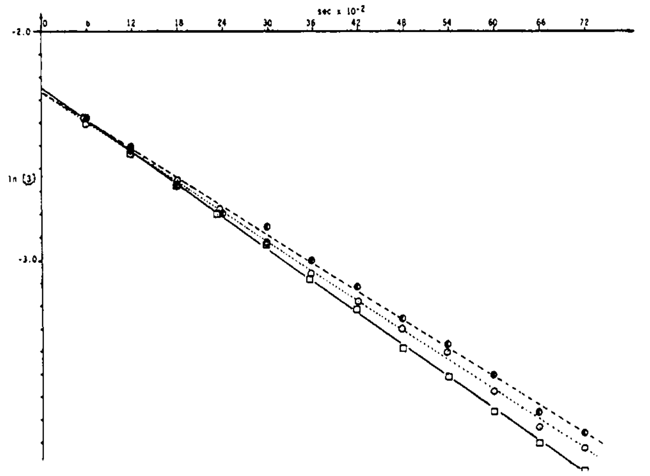
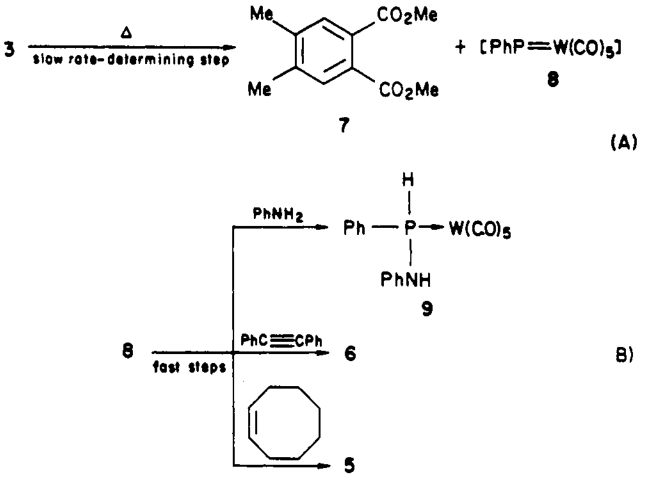


Figure 4. Kinetic data for the reactions of 3 with tolan and aniline at 117 °C (±1 °C) in perdeuterioxylene ($[3]_{t_0}$ = 0.1019 mol × L^{-1}, time in s): □, $[3]_{t_0}$:[PhC≡CPh] = 1:1, $k = 2.36 \times 10^{-4}$ s^{-1}, R = −0.9998; ○, $[3]_{t_0}$:[$PhNH_2$] = 1:1, $k = 2.16 \times 10^{-4}$ s^{-1}, R = −0.9990; ◐, $[3]_{t_0}$:[$PhNH_2$] = 1:2.3, $k = 2.08 \times 10^{-4}$ s^{-1}, R = −0.9989.

Scheme I



calculations[9]) then reacts very fast with the trapping reagents which have been especially chosen for their high efficiency. Of course, when replacing these electron-rich reagents by electron-poor species, the second step may become slower than the first one. In such a case, the overall yield decreases and byproducts resulting from the decomposition of 8 start to appear. It is interesting to note here that the decomposition path of the apparently analogous 7-silanorbornadienes is thought now to be a radical multistep process.[10] The different thermal behaviors of 7-phospha- and 7-silanorbornadienes may be ascribed (at least partly) to the fact that the P–C bonds are weaker than the Si–C bonds: E_m(Si–C) = 311 kJ mol^{-1} in $SiMe_4$[11] and E_m(P–C) = 276 kJ mol^{-1} in PMe_3,[11] thus favoring the simultaneous concerted cleavage of the two relatively labile heteroatom–carbon bonds in the phosphorus case.

In order to get some informations on the decomposition paths of 8, we have also studied the thermolysis of 3 without added trapping reagent. At 115 °C, this decomposition yields a complicated mixture of products. However, at 55 °C, when catalyzed by CuCl, this decomposition yields one main product. The structure of 10 was established by X-ray crystal structure analysis. Table I gives the atomic positional and thermal parameters with their estimated standard deviations for all atoms. The crystal structure of $[W(CO)_5]_3(PC_6H_5)_2$ consists of discrete mol-

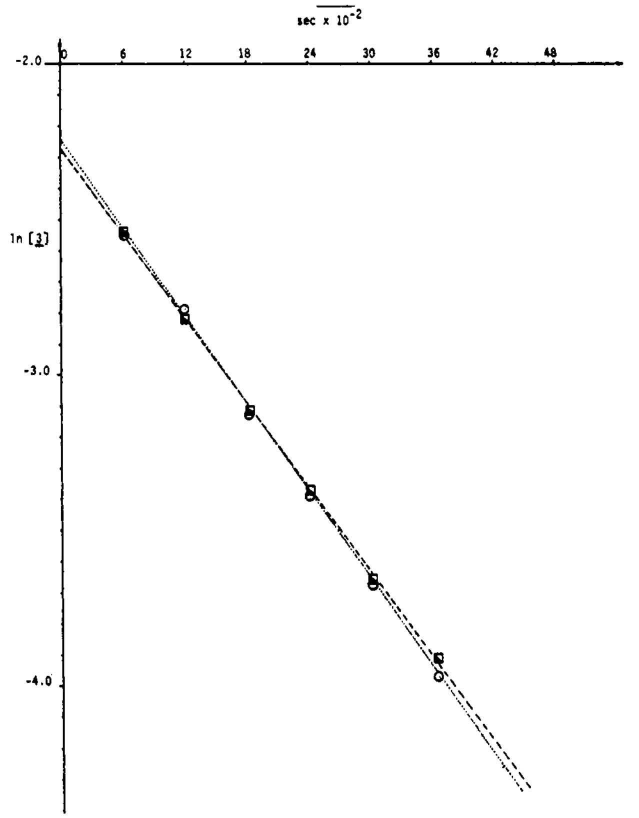


Figure 5. Kinetic data for the reactions of 3 with aniline and tolan at 125 °C (±1 °C) in perdeuterioxylene ($[3]_{t_0}$ = 1.1019 mol × L^{-1}; time in s): ○, $[3]_{t_0}$:[$PhNH_2$] = 1:1, $k = 4.80 \times 10^{-4}$ s^{-1}, R = −0.9993; ◩, $[3]_{t_0}$:[PhC≡CPh] = 1:2.3, $k = 4.57 \times 10^{-4}$ s^{-1} R = −0.9997.

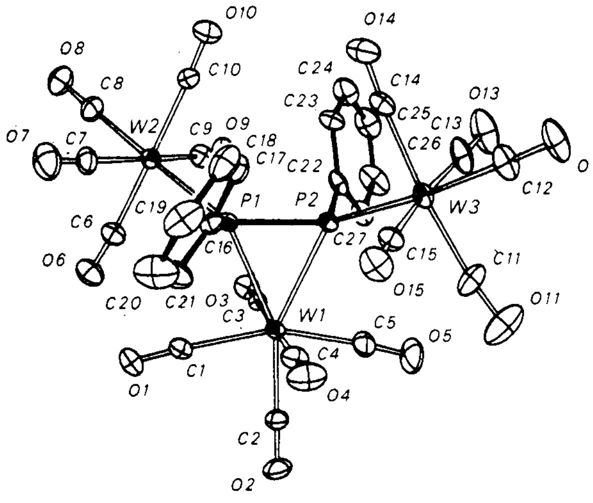
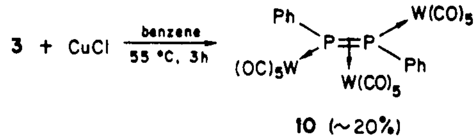


Figure 6. Structure of complex 10. The heavy-atom ellipsoids are scaled to enclose 30% of the electron density; hydrogen atoms are omitted.



10 (~20%)

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(9) Gonbeau, D.; Pfister-Guillouzo, G.; Marinetti, A.; Mathey, F. *Inorg. Chem.*

(10) Barton, T. J.; Goure, W. F.; Witiak, J. L.; Wulff, W. D. *J. Organomet. Chem.* **1982**, *225*, 87.

(11) O'Neill, M. E.; Wade, K. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. I, p 5.

Table I. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
W1	0.51072 (3)	0.81558 (2)	0.80788 (2)	3.074 (6)
C1	0.5724 (8)	0.8866 (6)	0.7182 (7)	4.9 (2)
O1	0.6074 (6)	0.9277 (5)	0.6691 (5)	7.3 (2)
C2	0.5486 (7)	0.9003 (6)	0.9031 (7)	4.7 (2)
O2	0.5699 (6)	0.9485 (5)	0.9524 (5)	7.5 (2)
C3	0.3761 (7)	0.8825 (5)	0.7977 (6)	4.3 (2)
O3	0.3079 (5)	0.9204 (4)	0.7960 (5)	6.0 (2)
C4	0.4473 (6)	0.7414 (5)	0.8952 (6)	3.7 (2)
O4	0.4088 (6)	0.7012 (4)	0.9427 (4)	5.5 (2)
C5	0.6528 (8)	0.7820 (7)	0.8505 (6)	5.4 (2)
O5	0.7318 (6)	0.7670 (7)	0.8793 (6)	9.8 (3)
W2	0.23093 (3)	0.66949 (2)	0.70195 (2)	3.560 (7)
C6	0.1910 (7)	0.7461 (6)	0.7963 (6)	4.5 (2)
O6	0.1614 (6)	0.7876 (5)	0.8479 (5)	6.7 (2)
C7	0.1679 (7)	0.7473 (7)	0.6096 (6)	5.1 (2)
O7	0.1295 (7)	0.7894 (6)	0.5595 (6)	8.4 (2)
C8	0.0973 (8)	0.6150 (7)	0.7034 (8)	5.7 (3)
O8	0.0211 (5)	0.5820 (6)	0.7043 (6)	8.2 (2)
C9	0.2799 (7)	0.5903 (6)	0.7991 (6)	4.9 (2)
O9	0.2989 (5)	0.5440 (4)	0.8530 (5)	6.4 (2)
C10	0.2690 (7)	0.5916 (6)	0.6057 (7)	4.8 (2)
O10	0.2855 (6)	0.5496 (5)	0.5512 (5)	7.7 (2)
W3	0.69411 (3)	0.67363 (2)	0.61295 (2)	3.679 (7)
C11	0.7996 (8)	0.7310 (8)	0.6908 (7)	6.4 (3)
O11	0.8661 (7)	0.7606 (7)	0.7300 (6)	11.0 (3)
C12	0.8044 (8)	0.6424 (6)	0.5421 (6)	5.7 (2)
O12	0.8675 (6)	0.6222 (5)	0.5003 (5)	8.2 (2)
C13	0.7273 (8)	0.5646 (7)	0.6741 (7)	6.5 (3)
O13	0.7484 (7)	0.5019 (5)	0.7007 (6)	10.3 (3)
C14	0.5999 (8)	0.6137 (5)	0.5239 (6)	4.3 (2)
O14	0.5541 (6)	0.5797 (5)	0.4711 (5)	7.2 (2)
C15	0.6762 (7)	0.7814 (5)	0.5467 (6)	4.1 (2)
O15	0.6724 (7)	0.8401 (4)	0.5066 (5)	6.5 (2)
P1	0.3994 (2)	0.7405 (1)	0.6871 (1)	3.02 (4)
C16	0.4037 (7)	0.8001 (5)	0.5882 (6)	3.8 (2)
C17	0.4285 (7)	0.7600 (6)	0.5138 (6)	4.8 (2)
C18	0.4307 (9)	0.8021 (8)	0.4348 (7)	6.6 (3)
C19	0.408 (1)	0.8851 (7)	0.4334 (7)	7.4 (3)
C20	0.379 (1)	0.9232 (8)	0.5043 (8)	8.8 (4)
C21	0.383 (1)	0.8831 (6)	0.5812 (7)	6.6 (3)
P2	0.5500 (2)	0.6904 (1)	0.7116 (1)	3.01 (4)
C22	0.5326 (7)	0.5945 (5)	0.7703 (6)	4.0 (2)
C23	0.4931 (8)	0.5277 (5)	0.7240 (6)	4.8 (2)
C24	0.4909 (9)	0.4514 (6)	0.7619 (8)	6.5 (3)
C25	0.5320 (9)	0.4395 (7)	0.8460 (8)	7.4 (3)
C26	0.571 (1)	0.5038 (7)	0.8917 (7)	7.4 (3)
C27	0.5754 (8)	0.5831 (6)	0.8552 (6)	4.8 (2)
HC17	0.4443	0.7028	0.5162	5[b]
HC18	0.4471	0.7742	0.3840	7[b]
HC19	0.4131	0.9156	0.3817	8[b]
HC20	0.3564	0.9785	0.5005	9[b]
HC21	0.3708	0.9132	0.6317	7[b]
HC23	0.4672	0.5346	0.6656	5[b]
HC24	0.4610	0.4062	0.7303	7[b]
HC25	0.5327	0.3860	0.8710	8[b]
HC26	0.5951	0.4957	0.9501	8[b]
HC27	0.6066	0.6274	0.8869	5[b]

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] These atoms were refined isotropically.

Table II. Selected Bond Lengths (Å), Angles (deg), and Averages with Their Estimated Standard Deviations

	Bond Lengths		
W1–P1	2.598 (2)	W1–P2	2.598 (2)
P1–W2	2.540 (2)	P2–W3	2.557 (2)
P1–P2	2.162 (3)	P2–C22	1.83 (1)
P1–C16	1.82 (1)		
W1–C1	2.03 (1)	W2–C9	2.05 (1)
W1–C2	2.05 (1)	W2–C10	2.05 (1)
W1–C3	2.08 (1)	W3–C11	2.00 (1)
W1–C4	2.04 (1)	W3–C12	1.96 (1)
W1–C5	2.02 (1)	W3–C13	2.04 (1)
W2–C6	2.02 (1)	W3–C14	2.04 (1)
W2–C7	2.04 (1)	W3–C15	2.03 (1)
W2–C8	1.98 (1)		
C1–O1	1.14 (1)	C9–O9	1.14 (1)
C2–O2	1.11 (1)	C10–O10	1.12 (1)
C3–O3	1.09 (1)	C11–O11	1.14 (1)
C4–O4	1.13 (1)	C12–O12	1.15 (1)
C5–O5	1.13 (1)	C13–O13	1.12 (1)
C6–O6	1.14 (1)	C14–O14	1.12 (1)
C7–O7	1.13 (1)	C15–O15	1.13 (1)
C8–O8	1.14 (1)		
	Bond Angles		
P1–W1–P2	49.19 (8)	P1–P2–W3	131.1 (1)
		P2–P1–W2	128.3 (1)
W1–P1–P2	65.41 (9)	P1–P2–C22	104.9 (3)
W1–P2–P1	65.40 (9)	P2–P1–C16	105.0 (3)
W1–P1–W2	126.96 (9)	P1–W1–C2	158.0 (3)
W1–P2–W3	128.40 (9)	P2–W2–C2	152.8 (3)
P1–W1–C3	75.8 (3)	P1–W1–C4	87.8 (3)
P2–W1–C3	124.9 (3)	P2–W1–C4	91.9 (3)
P1–W1–C1	90.4 (3)	P2–W1–C5	75.8 (3)

Phenyl Rings: mean C–C = 1.379 (5) Å; mean C–C–C = 119.9 (3) Å

ecules only linked by van der Waals contacts; there are no unusual intermolecular contacts. Figure 6 displays one molecule of **10**. Table II gives selected bond lengths and angles with averages and estimated standard deviations. The overall crystal structure of **10** is close to that of the corresponding chromium complex determined by Borm, Zsolnai, and Huttner.[12] As in the chromium complex W1 is heptacoordinated with five carbonyl moieties and the double P═P bond whereas W2 and W3 are hexacoordinated by five carbonyl groups and one phosphorus atom. The P_2W triangle is isocel, and the P1–W1–P2 bond angle of 49.19 (8)° is close to the values found in the chromium triangles (49.6 (1) and 49.6 (1)°). The P1–P2 bond length of 2.162 (3) Å is significantly shorter than normal single P–P bond lengths (2.20–2.25 Å) but also significantly longer than the P═P bond length of 2.03 Å found in $[Cr(CO)_5]_2(PC_6H_5)_2$.[12] This is not surprising, the P═P double bond being π-bonded to a $W(CO)_5$ fragment. Probably due to the different electronic and steric behaviors of the $W(CO)_5$ and $Cr(CO)_5$ moieties, the P1–P2 bond in the tungsten complex is 0.037 Å longer than in the chromium complex. The P–C bond length of 1.823 (7) Å (mean) has a normal value for a single P–C bond. Also the two P1–W2 and P2–W3 bond lengths are not significantly different with a normal mean value of 2.548 (2) Å. The absolute value of the C16–P1–P2–C22 torsional angle is equal to 151.5°, quite different from that found in the chromium complex (127.8 and 123.5°) probably due to different steric interactions. The $W(CO)_5$ moieties and the phenyl rings have normal geometries as seen from the data of Table II.

At least formally, the structure of **10** results from a classical carbene-like dimerization of the terminal phosphinidene complex **8**. However, a part of **8** must follow another decomposition path including the breaking of the phosphorus–tungsten bond with the release of one $W(CO)_5$ unit which is used for the π-complexation of the P═P double bond of **10**.

Experimental Section

NMR spectra were recorded on a Bruker WP 80 instrument at 80.13 MHz for ^1H and 32.435 MHz for ^{31}P. Chemical shifts

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[12] Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 977.

are reported in parts per million from external 85% H_3PO_4 for ^{31}P. Downfield shifts are noted positive. IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer. Mass spectra were recorded on a VG 30 F spectrometer by Service Central d'Analyse du CNRS (Lyon). All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh Riedel de Haën).

(1,2,3-Triphenylphosphirane)pentacarbonyltungsten (Trans Isomer 4). Complex **3** (1.5 g, 2.3 mmol) and *trans*-stilbene (1.03 g, 5.7 mmol) were heated at 115 °C for 5 h in xylene (30 mL). After evaporation, the residue was chromatographed with hexane–toluene (90:10): $R_f \sim 0.7$; yield, 1.07 g (76%) of **4**. Complex **4** was characterized by ^{31}P and ^1H NMR (see ref 3).

(9-Phenyl-9-phosphabicyclo[6.1.0]nonane)pentacarbonyltungsten (5a,b). Complex **3** (1.5 g, 2.3 mmol) and cyclooctene (0.8 mL, 6.1 mmol) were heated at 115 °C for 7 h in xylene (30 mL). After evaporation, the residue was chromatographed with hexane: $R_f \sim 0.6$; yield, 1.0 g (79%) of a mixture **5a,b**. Complexes **5a,b** were characterized by ^{31}P NMR (see ref 3).

Phosphirane Complex 4 as a Generator of a Terminal Phosphinidene Complex. Complex **4** (0.25 g, 0.4 mmol) was heated with diphenylacetylene (0.22 g, 1.2 mmol) in toluene at 150 °C for 3 h in a sealed tube. After evaporation, the residue was chromatographed with hexane: $R_f \sim 0.5$; yield, 0.1 g (41%) of **6** (see ref 5).

Kinetic Experiments. Reaction rates were determined by single-scan proton NMR spectroscopy. Spectra were run on a SY WP 80 Bruker spectrometer every 10 min with a digital resolution of 0.12 Hz. The concentration of compound **3** at the time *t* was measured by integration of the methoxy signal of **3** and methoxy signal of **7**.

$$[3]_t = [3]_{t_0} \frac{\text{integration } \mathbf{3}}{\text{integration } \mathbf{3} + \text{integration } \mathbf{7}}$$

The constancy of the temperature is ±0.1 °C during all the series of measurements, but the accuracy of the temperature is not better than ±1 °C according to the calibration experiments.

Complex 10. Complex **3** (2.5 g, 3.8 mmol) and CuCl (0.3 g, 3 mmol) were heated at 55 °C in benzene for 3 h. After evaporation, the residue was chromatographed with hexane–toluene (60:40): $R_f \sim 0.4$; yield, 0.3 g (20%) of red solid. Complex **10** was crystallized in CH_2Cl_2: ^{31}P NMR (CH_2Cl_2) δ −20.6; mass spectrum (chemical ionization, ^{184}W), *m/e* (relative intensity) 865 (M − $W(CO)_5$ + 1, 41), 353 ($W(CO)_6$ + 1, 11), 79 (100); IR ($CDCl_3$) ν(CO) 2100 (m), 2070 (s), 2010 (sh), 2000 (s), 1950 (vs) cm^{-1}. Anal. Calcd for $C_{27}H_{10}W_3O_{15}P_2$: C, 27.30; H, 0.85. Found: C, 27.48; H, 0.87.

X-ray Data Collection and Processing. Suitable single crystals of **10** were obtained by slow evaporation of CH_2Cl_2 solutions at room temperature. A systematic search in reciprocal space using a Philips PW 1100/16 automatic diffractometer showed that crystals of **10** belong the the monoclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Mo Kα radiation (λ = 0.71073 Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{27}H_{10}O_{15}P_2W_3$, mol wt 1188; a = 13.264 (2) Å, b = 16.222 (3) Å, c = 15.531 (3) Å, β = 94.50 (2)°; V = 3331 Å^3; Z = 4, d_{calcd} = 2.368 g cm^{-3}, d_{obsd} = 2.34 ± 0.02 g cm^{-3}; μ = 107.2 cm^{-1}; F_{000} = 2176; space group $P2_{1/n}$, a non-standard setting of $P2_{1/c}$.

A parallelepipedic crystal of 0.28 × 0.27 × 0.12 mm was sealed in a Lindemann glass capillary and mounted on a rotation free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step–scan used was $\Delta\theta = 1.0 + (\text{Mo K}\alpha_1,\alpha_2$ splitting) with a step width of 0.05° and a scan speed of 0.032° s^{-1}. A total of 6398 *hkl* and $hk\bar{l}$ reflections were recorded (3° < θ < 25°). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used,[13] with the exception of a local data reduction program.

Three standard reflections measured every hour during the entire data collection period showed no significant trend.

The raw step–scan data were converted to intensities using the Lehmann–Larson method[14] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the numerical integration method of Busing and Levy[15] (transmission factors between 0.08 and 0.29). A unique data set of 3981 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved by using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of B_{eqv}(C) + 1 Å^2 but not refined. Full least-squares refinement converged to $R(F)$ = 0.027 and $R_w(F) = 0.041(\sigma(F^2) = [\sigma^2_{\text{count}} + (pI)^2]^{1/2})$. The unit-weight observation was 0.90 for p = 0.06. A final difference map revealed no significant maxima. The scattering factors coefficients and anomalous dispersion coefficients come respectively from ref 16 and 17.

Registry No. **3**, 82265-64-3; **4**, 88000-33-3; **5a**, 88081-26-9; **5b**, 88000-31-1; **6**, 82265-68-7; **10**, 98735-41-2; CuCl, 7758-89-6; aniline, 62-53-3; tolan, 501-65-5; cyclooctene, 931-88-4; *trans*-stilbene, 103-30-0.

Supplementary Material Available: Table III, anisotropic thermal parameters for anisotropic atoms, and Table IV, listings of observed and calculated structure factors for all observed reflections (20 pages). Ordering information is given on any current masthead page.

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(16) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 b.

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