Generation and Chemical Trapping of (1,2-Ethanediphosphinidene)tetracarbonyltungsten

Claude Charrier, Nicole Maigrot, and François Mathey*

Laboratoire CNRS-SNPE, BP No. 28, 94320 Thiais, France

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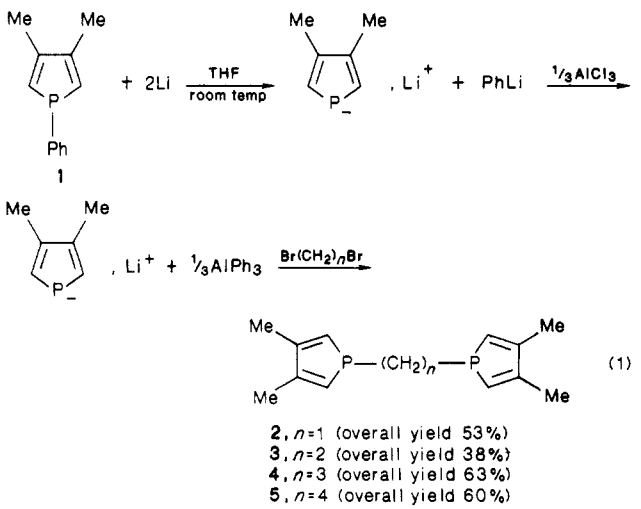
A series of 1,*n*-bis(3,4-dimethylphospholyl)alkanes has been synthesized by reaction of (3,4-dimethylphospholyl)lithium with 1,*n*-dibromoalkanes. The cleavage of these bis(phospholyl)alkanes by lithium in THF generally affords pure (3,4-dimethylphospholyl)lithium that has been characterized for the first time by ^1H and ^{13}C NMR spectroscopy. However, when $n = 3$, the cleavage of the 1,3-bis(phospholyl)propane leads to a phosphabicyclo[3.3.0]octene that results from the intramolecular cyclization of a transient 1-(3-lithiopropyl)phosphole by addition of the carbanion onto the phosphole dienic system. The 1,2-bis(3,4-dimethylphospholyl)ethane reacts with $W(CO)_6$ at 130 °C to give the *P,P'*-$W(CO)_4$ chelate complex. This complex in turn reacts with dimethyl acetylenedicarboxylate to give cleanly the corresponding [1,2-bis-(7-phosphanorbornadien-7-yl)ethane]tetracarbonyltungsten complex through [4 + 2] cycloaddition with the dienic systems of the two phosphole rings. This new complex is an efficient generator of (1,2-ethanediphosphinidene)tetracarbonyltungsten, $\overline{P—CH_2—CH_2—P=W}(CO)_4$, at 130 °C in toluene. This diphosphinidene complex has been trapped by methanol, diethylamine, tolan, and cyclooctene to give a series of new $W(CO)_4$ complexes including the first known 1,2-bis(phosphirenyl)- and bis(phosphiranyl)ethane derivatives.

In a series of recent papers, we have demonstrated that transient phosphinidene complexes [R—P=$M(CO)_5$] (M = Cr, Mo, W) as generated by thermal decomposition of the appropriate 7-phosphanorbornadiene complexes have a rich and versatile chemistry. Indeed, they readily insert into O–H,[1] N–H,[1] and some activated C–H bonds,[2] and they form three-membered rings with C=C[3] and C≡C[4] multiple bonds. The experiments were conducted with some simple R substituents at phosphorus such as methyl and phenyl. In a subsequent step, we started to investigate the chemistry of terminal phosphinidene complexes with functional alkyl[5,6] and alkoxy groups[7] and noted some interesting variations in the reactivity of these species[7] and some original rearrangements.[5,6] As a logical further step in this program, we present here our work on the generation and chemical properties of the first reported chelating diphosphinidene $\overline{P—CH_2—CH_2—P=W}(CO)_4$.

Results and Discussion

Our general aim was to study the properties of P–$(CH_2)_n$–P $\eta^1(P),\eta^1(P')$-complexes. According to our previously established route to terminal phosphinidene complexes,[1-4] the necessary starting points for building generators of such species were the still unknown 1,*n*-bis(3,4-dimethylphospholyl)alkanes. These compounds were prepared according to eq 1. The yields of **2–5** from **1** are calculated for the chromatographed products. The lower yield of **3** is due to a higher sensitivity of this phosphole toward oxidation during the purification procedure and not to the appearance of side products during the synthesis in this particular case. Similar 1,*n*-bis(2,3,4,5-tetraphenylphospholyl)alkanes had been previously reported by Braye,[8] but these phospholes are useless for our purpose since their dienic systems are deactivated by the phenyl substitution. Having at hand these new 1,*n*-bis(phospholyl)alkanes, we decided to investigate their properties a little bit further before going on with our initial program. Through the cleavage of their two exocyclic P–C bonds by lithium, these species might be used as convenient starting points for the synthesis of 1,*n*-dilithioalkanes (eq 2). We thus attempted to cleave these bonds, and, contrary to our expectations, we observed the consumption of only 2 equiv of lithium/rmol of bis(phospholyl)alkane instead of 4. When $n = 1$, 2, and 4, the end product was pure (3,4-dimethylphospholyl)lithium (**6**) (eq 3). Obviously, the weakly aromatic transient 1-(ω-lithioalkyl)-3,4-dimethylphosphole **7** decomposed very rapidly to give the highly aromatic phospholyl anion[9] and volatile hydrocarbon by products. This result offered us the opportunity to characterize more fully the phospholyl anion **6**. Indeed up to now, such species have been characterized only by their ^{31}P NMR spectra.[10,11] Undoubtedly this is due to the fact that they had never been obtained in the pure state previously. A pure solution of **6** in perdeuteriotetrahydrofuran was analyzed by ^1H, ^{13}C, and ^{31}P NMR



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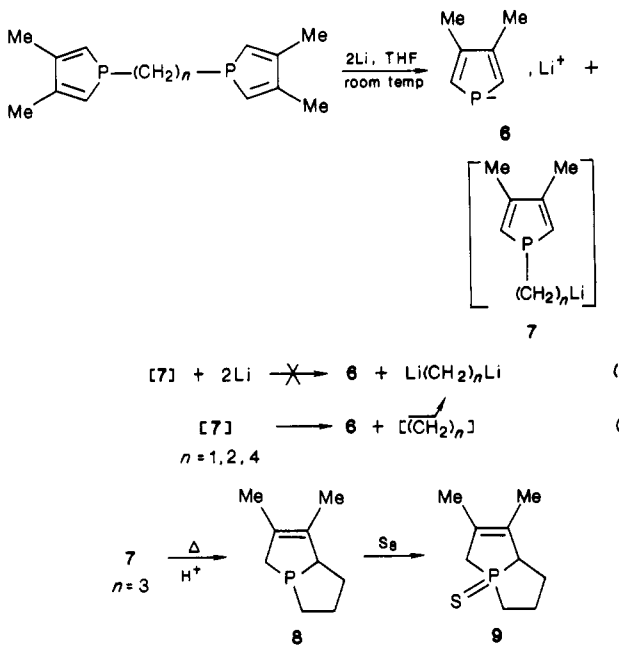
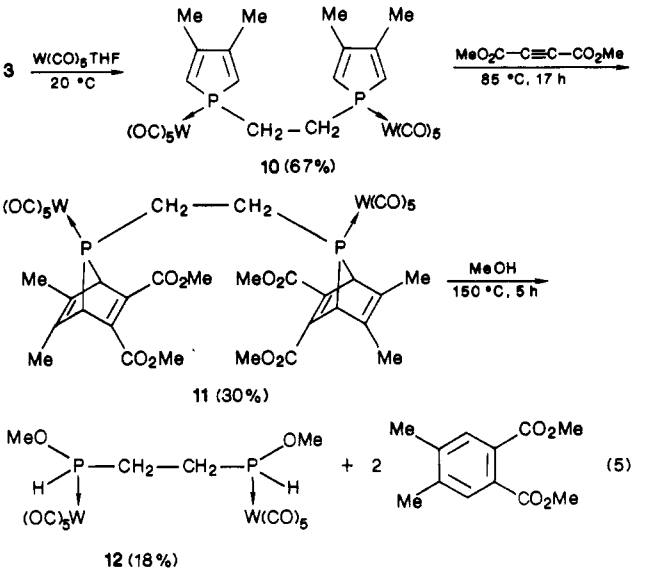


spectroscopy. The ^1H NMR data are surprisingly similar to those of a 3,4-dimethyl-substituted phosphole: **6** (C_4D_8O), δ 1.98 (s br, 6 H, Me), 6.22 (d br, ^2J(H–P) = 39.5 Hz, 2 H, =CH); **1** ($CDCl_3$), δ 1.91 (dd, 6 H, Me), 6.36 (dd, ^2J(H–P) = 38 Hz, 2 H, =CH). On the contrary, the ^{13}C NMR spectrum of **6** shows one very characteristic feature. The intracyclic ^1J(C–P) coupling constant is huge (45 Hz), whereas it is low in tervalent phospholes[12] (e.g., 7.3 Hz for **1**). There is here an obvious similarity with phosphaalkenes in which the doubly bonded phosphorus and carbon are strongly coupled[13] [e.g., 43.5 Hz for mesityl(diphenylmethylene)phosphine]. This result is a consequence of the high electronic cyclic delocalization within **6** that imparts some double-bond character to the P–C bonds of the phospholyl ring. When n = 3, the corresponding 1-(lithioalkyl)-3,4-dimethylphosphole **7** decomposes via a different route. The carbanionic side chain attacks the phosphole dienic system to give an original bicyclic phosphine **8** that has been characterized as its *P*-sulfide **9** (eq 4). The formula of **9** has been established by elemental analysis and by exact mass measurement (calcd 186.0631, found 186.063 56). The ^1H NMR spectrum indicates the absence of vinylic proton, and the ^{13}C NMR spectrum shows two inequivalent methyls, four methylene groups, one CH group, and two inequivalent fully substituted vinylic carbons. A similar addition of *n*-butyllithium onto the dienic system of 1-*n*-butyl-3,4-dimethylphosphole has already been described in the literature.[14]

Coming back to our initial programm, we then turned our attention toward the synthesis of 1,*n*-bis(7-phosphanorbornadien-7-yl)alkanes. Following the general scheme, we first allowed **3** to react with an excess of $W(CO)_5THF$ and obtained the expected complex **10** in fair yield. Then **10** was converted into the corresponding 7-phosphanorbornadiene complex **11** by reaction with dimethyl acetylenedicarboxylate. Unfortunately, the yield of this conversion was poor. Finally, in order to check the efficiency of **11** as a generator of $[(OC)_5W{=}P{-}CH_2{-}CH_2{-}P{=}W(CO)_5]$, we performed its decomposition in the presence of an excess of methanol (eq 5). The yield of this trapping reaction appeared to be very poor. Thus it was quite obvious that this classical scheme was of no practical use.



In our initial work on the synthesis of 7-phosphanorbornadiene complexes,[15] we showed that the steric bulk of the substituent at phosphorus had a strong adverse effect on the yield of the Diels–Alder cycloaddition between the phosphole complex and dimethyl acetylenedicarboxylate. Thus, we thought that the main reason for the low yield of **11** lay in the poor accessibility of the two sides of the dienic systems of **10**. Consequently, we decided to replace the P,P complex **10** by the chelate complex **13** for which one side of both dienic systems is well exposed to external attack. This proved to be a good choice (eq 6). That the dienic systems of **13** are quite reactive was immediately obvious when we performed the complexation of **3** by an excess of $W(CO)_6$: in this case, besides **13**, we obtained the bimetallic complex **14** in which one of the dienes is π-complexed. The reaction of **13** with dimethyl acetylenedicarboxylate proceeded much more rapidly than the reaction of **10** and gave a much better yield of the 7-phosphanorbornadiene chelate **15**. According to its ^{31}P NMR spectrum, **15** is symmetrical with two equivalent phosphorus atoms ($\delta(^{31}P)$ +244.4 in C_6D_6, $^1J(^{31}P{-}^{183}W)$ = 232 Hz). Moreover, the attack of the alkyne has taken place on the sides of the dienes that are at the opposite of the $W(CO)_4$ moiety as evidenced by the very low ^2J(C–P) couplings of the vinylic carbons bearing the CO_2Me groups ($\delta(CCO_2Me)$ 146.37 in C_6D_6, ^2J(C–P) $\simeq$ 2.4 Hz). These low couplings are correlated with the =C—C—P—W dihedral angles and are characteristic of this stereochemistry.[5] **15** is practically the only isomer formed in this reaction according to the ^{31}P NMR spectrum of the crude reaction mixture. The thermal decomposition of **15** at ca. 120–130 °C proved to be an excellent method for generating the unstable (1,2-ethanediphosphinidene)-tetracarbonyltungsten (**16**) (eq 7). This diphosphinidene complex has the same varied chemistry as the more classical terminal monophosphinidene complexes (eq 8–11). Apparently, the reaction with methanol gives a single isomer of **17** according to the ^{31}P NMR spectrum ($\delta(^{31}P)$ +138.35 in C_6D_6, ^1J(P–H) = 350 Hz). However, the ^{31}P-decoupled ^1H NMR spectrum shows two singlets in a 1:1 ratio at 3.02 and 3.08 ppm in C_6D_6 for the methoxy groups

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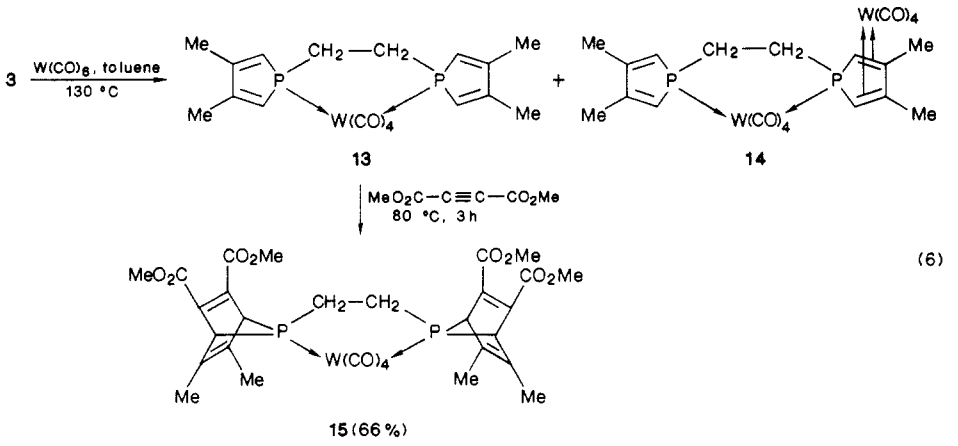
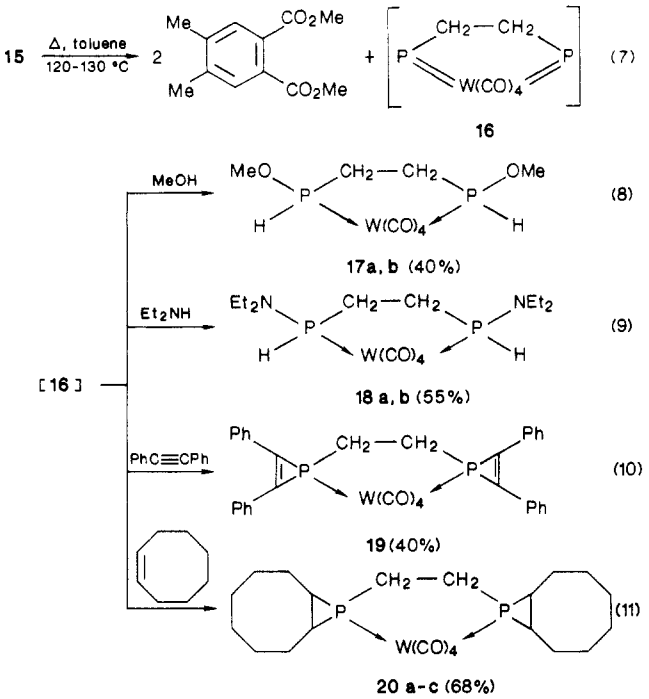
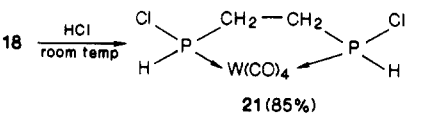


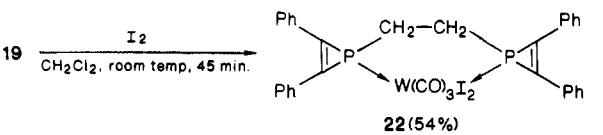


after decoupling of the P–H protons. Thus **17** is in fact a mixture of two isomers with identical ^{31}P chemical shifts. On the contrary, the two isomers of **18** (1:1 ratio) give distinct signals in the ^{31}P NMR spectrum ($\delta(^{31}P)$ +67.24 and +65.66 in C_6D_6, ^1J(P–H) = 340 Hz in both cases). As expected, **19** gives a single ^{31}P peak at high field (δ −115.13 in $CDCl_3$) whereas **20** is a mixture of the three possible isomers (two singlets at −126.27 and −133.95 ppm in C_6D_6 for the two symmetrical isomers and a AB system at −126.3 and −132.0 ppm with a J(P-P) coupling of 29.3 Hz for the single unsymmetrical isomer). These isomers correspond to the various stereochemical dispositions of the two eight-membered rings. If we place the P–CH_2–CH_2–P bridge in the upper position and the $W(CO)_4$ complexing group in the lower position, the two symmetrical isomers correspond to the up,up and down,down dispositions of the eight-membered rings and the unsymmetrical isomer to the up,down or down,up dispositions. The observed ratios of ca. 1:1:2 are equal to the statistical ratios, showing that there is no steric hindrance leading to a preferential stereochemistry.

This series of new products offers a wide range of synthetic possibilities. Indeed, numerous reactions can be performed either at phosphorus or at tungsten. For example, the reaction of HCl with **18** yields the new complex **21** that derives from the unknown and potentially versatile Cl(H)P–CH_2–CH_2–P(H)Cl ligand (eq 12). On the other



hand, iodine converts **19** into the tungsten(2+) complex **22** (eq 13). The ^{31}P NMR spectrum demonstrates that



the phosphirene ring is still intact in **22** ($\delta(^{31}P)$ −114.38 in $CDCl_3$), and elemental C, H, I, P, and W analysis establishes the composition of the complexing group. This reaction shows that it is possible to develop the analogue of the rich chemistry of the (diphos)W moiety in which the PPh_2 groups would be replaced by the very strained P—C(Ph)=C(Ph) rings that impart special properties to the phosphorus atoms (very low Tolman cone angles, high s character of the lone pairs, etc. ...). It must be pointed out here that even a powerful ligand such as 2,2′-bipyridyl is unable to displace the diphosphirene from the coordination sphere of tungsten in **22** and that it seems difficult to use **19** or **22** as sources of the free ligand.

We then tried to generalize this kind of chemistry in two directions. First, we decided to check if it was possible to change the length of the P–$(CH_2)_n$–P bridge. We immediately found that it was impossible to conveniently prepare the $CH_2P_2W(CO)_4$ chelate derived from **2** probably because this phosphole has a low thermal stability. On the other hand, we were able to duplicate the chemistry of **3** with **4**, but the yields of the reactions were uniformly much lower (eq 14). The only point that deserves some comments concerns the influence of the length of the chain on the ^{31}P chemical shifts of the chelates. Whereas **24** and **25** resonate in the same range as their acyclic analogues (e.g., **24**, +216.13 ppm, and **25**, −158.0 ppm, in $CDCl_3$; PhP→$W(CO)_5$ analogues, +208.0[15] and −161.4[4] ppm in toluene), the products with the P–CH_2–CH_2–P bridge resonate at much lower fields (**15**, +244.4 ppm in C_6D_6; **19**, −115.13 ppm in $CDCl_3$). This trend is characteristic of the five-membered P–CH_2–CH_2–P–M rings (M = $Cr(CO)_4$, $Mo(CO)_4$, $W(CO)_4$) and has already been noted by others on a series of diphos complexes.[16]

Finally, we also tried to replace the $W(CO)_4$ complexing

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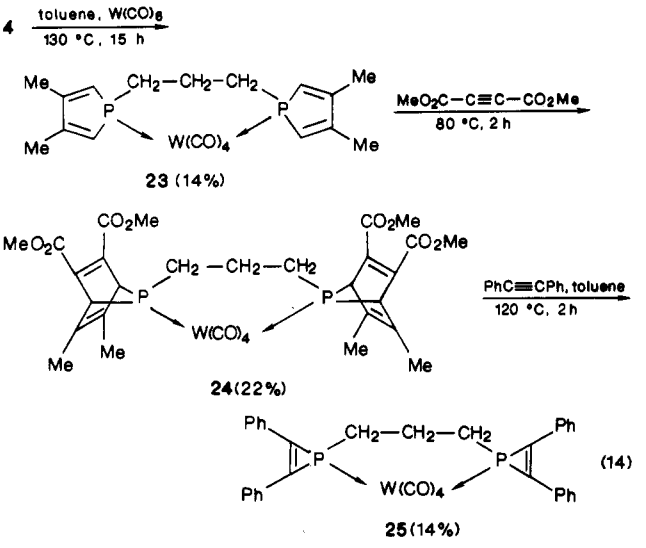
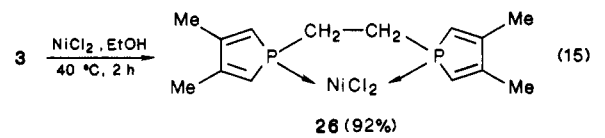


group by other metallic moieties. According to our previous work in this area, $Cr(CO)_4$ and $Mo(CO)_4$ very likely behave as $W(CO)_4$. Thus we chose to replace $W(CO)_4$ by the more heterogeneous $NiCl_2$ in order to get more significant information. The corresponding diamagnetic complex of **3** was easily obtained (eq 15) and fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Unfortunately, we were unable to prepare the corresponding 7-phosphanorbornadiene complex by reaction of **26** with dimethyl acetylenedicarboxylate. Apparently, $NiCl_2$ is unable to stabilize the 7-phosphanorbornadiene skeleton in spite of the favorable chelate effect.



Experimental Section

All reactions were carried out under argon. Solvents and silica gel (70–230 mesh Merck) were used after being degassed with argon. NMR spectra were recorded on a Bruker WP 80 spectrometer at 80.13 MHz for ^1H, 32.43 MHz for ^{31}P, and 20.15 MHz for ^{13}C spectra. ^{31}P chemical shifts are externally referenced to 85% H_3PO_4; ^1H and ^{13}C chemical shifts are internally referenced to Me_4Si and are positive for downfield shifts in all cases. IR spectra were recorded on a Perkin-Elmer 297 spectrometer and mass spectra on a Shimadzu GCMS-QP1000 spectrometer.

General Procedure for the Synthesis of 1,*n*-Diphospholylalkanes. A mixture of 1-phenyl-3,4-dimethylphosphole (18.8 g, 0.1 mol) and lithium in thin pieces (1.4 g, 0.2 mol) in THF (200 mL) was stirred at room temperature. The solution became rapidly dark red, and the reaction was complete when lithium had disappeared (about 3 h). After the solution was cooled to −30 °C, $AlCl_3$ (2.2 g, 0.017 mol) was added and the mixture stirred 1 h while the temperature was raised slowly to 20 °C. A solution of 1,*n*-dibromoalkane (0.05 mol) and THF (50 mL) was added to the phospholyllithium at 20 °C. After evaporation the residue was chromatographed on silica gel (500 g) with toluene/hexane (20:80).

Bis(3,4-dimethylphospholyl)methane (2): mp 90 °C; ^1H NMR ($CDCl_3$) δ 2.10 (CH_2), 2.06 ($^4J_{HP}$ = 3.0, $^4J_{HH}$ = 1.0 Hz, CH_3), 6.32 ($^2J_{HP}$ = 38.0 Hz, :CH); ^{31}P NMR ($CDCl_3$) δ −13.37; ^{13}C NMR ($CDCl_3$) δ 16.23 ($^1J_{CP}$ = 30.0 Hz, CH_2), 17.32 (CH_3), 129.83 (:CH), 148.13 (:C–). Anal. Calcd for $C_{13}H_{18}P_2$: C, 66.10; H, 7.63; P, 26.27. Found: C, 66.40; H, 7.69; P, 25.82.

1,2-Bis(3,4-dimethylphospholyl)ethane (3): mp 54 °C; ^1H NMR ($CDCl_3$) δ 1.67 (CH_2), 2.05 ($^4J_{PH}$ = 3.0 Hz, CH_3), 6.25 ($^2J_{HP}$ = 38.0 Hz, :CH); ^{31}P NMR ($CDCl_3$) δ −3.96; ^{13}C NMR ($CDCl_3$) δ 17.26 (CH_3), 20.30 (CH_2), 127.83 (:CH), 148.37 (:C–). Anal. Calcd for $C_{14}H_{20}P_2$: C, 67.18; H, 8.06; P, 24.75; Found: C, 66.76; H, 8.08; P, 23.05.

1,3-Bis(3,4-dimethylphospholyl)propane (4): oil; ^1H NMR ($CDCl_3$) δ 1.60 (CH_2), 2.03 ($^4J_{HP}$ = 3.0, $^4J_{HH}$ = 0.8 Hz, CH_3), 6.29 ($^2J_{HP}$ = 38.0 Hz, :CH); ^{31}P NMR ($CDCl_3$) δ −8.4; ^{13}C NMR ($CDCl_3$) δ 16.75 ($^3J_{CP}$ = 3.7 Hz, CH_3), 24.45 ($^1J_{CP}$ = 17.0, $^3J_{CP}$ = 8.5 Hz, P–CH_2), 24.60 ($^2J_{CP}$ = 7.0 Hz, C–CH_2–C), 128.13 ($^1J_{CP}$ = 4.9 Hz, :CH), 147.10 ($^2J_{CP}$ = 7.3 Hz, :C–). Anal. Calcd for $C_{15}H_{22}P_2$: C, 68.18; H, 8.33; P, 23.48. Found: C, 68.12; H, 8.31; P, 23.44.

1,4-Bis(3,4-dimethylphospholyl)butane (5): mp 72 °C; ^1H NMR ($CDCl_3$) δ 1.60 (CH_2), 2.08 ($^4J_{HP}$ = 3.0 Hz, CH_3), 6.30 ($^2J_{HP}$ = 38.0 Hz, :CH); ^{31}P NMR ($CDCl_3$) δ −7.43; ^{13}C NMR ($CDCl_3$) δ 17.35 ($^3J_{CP}$ = 3.7 Hz, CH_3), 23.20 ($^1J_{CP}$ = 14.6 Hz, P–CH_2), 28.53 ($^2J_{CP} \simeq {}^3J_{CP} \simeq$ 8.0 Hz, C–CH_2), 128.76 ($^1J_{CP}$ = 3.6 Hz, :CH), 147.85 ($^2J_{CP}$ = 7.3 Hz, :C–). Anal. Calcd for $C_{16}H_{24}P_2$: C, 69.06; H, 8.63; P, 22.30. Found: C, 69.12; H, 8.86; P, 21.31.

(3,4-Dimethylphospholyl)lithium (6). A mixture of **3** (2.50 g, 0.01 mol) and lithium ribbon (0.14 g, 0.02 mol) in 20 mL of dry THF was stirred at room temperature. The reaction was complete when lithium had disappeared (about 2 h). The solvent was evapoarated, and the brown yellow powder was dissolved in tetrahydrofuran-d_8: ^1H NMR δ 1.98 (CH_3), 6.22 ($^2J_{HP}$ = 39.5 Hz, :CH); ^{31}P NMR δ 59.03; ^{13}C NMR δ 17.43 (CH_3), 128.63 ($^1J_{CP}$ = 45.0 Hz, :CH), 127.99 (J_{CP} = 2.0 Hz, :C–).

3,4-Dimethyl-1-phosphabicyclo[3.3.0]-3-octene (8). A mixture of **4** (2.64 g, 0.01 mol) and lithium ribbon 0.14 g, 0.02 mol) in 20 mL of dry THF was stirred at room temperature. The reaction was complete when lithium had disappeared (about 2 h). After hydrolysis with 1 mL of H_2O, solvents were evaporated and the residue was chromatographed on silica gel (200 g) with toluene/hexane (20:80). Compound **8** was recovered in 31% yield as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.62 (CH_3), 1.3–3.3 (CH and CH_2); ^{31}P NMR ($CDCl_3$) δ −29.33; ^{13}C NMR ($CDCl_3$) δ 14.66 ($^3J_{CP}$ = 1.0 Hz, CH_3), 16.47 ($^3J_{CP}$ = 0 Hz, CH_3), 24.59 ($^2J_{CP}$ = 4.9 Hz, CH_2), 29.30 ($^1J_{CP}$ = 13.5 Hz, CH_2), 32.65 ($^2J_{CP}$ = 0 Hz, CH_2), 39.25 ($^1J_{CP}$ = 14.7 Hz, CH_2), 52.79 ($^1J_{CP}$ = 8.6 Hz, CH), 131.22 ($^2J_{CP}$ = 2.5 Hz, :C–), 132.31 ($^2J_{CP}$ = 2.5 Hz, :C–).

3,4-Dimethyl-1-phosphabicyclo[3.3.0]-3-octene 1-Sulfide (9) was prepared by the same procedure as for **8**. After hydrolysis with 1 mL of water, an excess of sulfur, S_8 (0.5 g), was added, and the medium was stirred at room temperature for 15 h. After evaporation, the residue was chromatographed on silica gel (200 g) with toluene. Compound **9** was recovered in 38% yield (mp 66 °C): ^1H NMR ($CDCl_3$) δ 1.69 (CH_3), 1.3–2.82 (CH and CH_2); ^{31}P NMR ($CDCl_3$) δ 67.39; ^{13}C NMR ($CDCl_3$) δ 14.02 ($^3J_{CP}$ = 11.0 Hz, CH_3), 16.17 ($^3J_{CP}$ = 12.2 Hz, CH_3), 23.87 ($^2J_{CP}$ = 7.3 Hz, CH_2), 29.77 ($^2J_{CP}$ = 8.6 Hz, CH_2), 35.41 ($^1J_{CP}$ = 47.6 Hz, CH_2), 44.86 ($^1J_{CP}$ = 47.6 Hz, CH_2), 54.16 ($^1J_{CP}$ = 53.7 Hz, CH), 128.65 ($^2J_{CP}$ = 6.1 Hz, :C–), 130.95 ($^2J_{CP}$ = 8.5 Hz, :CH). Anal. Calcd for $C_9H_{15}PS$: C, 58.04; H, 8.12; P, 16.62. Found: C, 58.13; H, 8.26; P, 16.55.

[η^1(P),η^1(P′)-1,2-Bis(3,4-dimethylphospholyl)ethane]decacarbonylditungsten (10). Complex **10** was prepared by allowing diphosphine **3** (2.50 g, 0.01 mol) to react with $W(CO)_5THF$[17] (0.02 mol) at room temperature for 30 min. The solvent was evaporated, and the complex was crystallized in toluene (67% yield: mp 265 °C dec): ^1H NMR ($CDCl_3$) δ 1.84 ($^2J_{HP}$ = 2.7 Hz, CH_2), 2.16 ($^4J_{HH}$ = 0.7 Hz, CH_3) 6.19 ($^2J_{HP}$ = 37.0 Hz, :CH); ^{31}P NMR δ 4.24; ^{13}C NMR ($CDCl_3$) δ 17.20 (CH_3), 25.62 (CH_2), 127.41 (:CH), 155.55 (:C–), 195.87 (CO eq), 198.71 (CO ax); IR (decaline) ν(CO) 2065 (m) and 1940 (vs) cm^{-1}; mass spectrum (200 °C), *m/e* (relative intensity) 898 (M, 37). Anal. Calcd for $C_{24}H_{20}O_{10}P_2W_2$: C, 32.07; H, 2.23; P, 6.90. Found: C, 32.72; H, 2.26; P, 6.58.

{η^1(P),η^1(P′)-1,2-Bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadien-7-yl]ethane}decacarbonylditungsten (11). Complex **10** (4.49 g, 0.005 mol) and dimethyl acetylenedicarboxylate (2.4 mL, 0.02 mol) were heated at 85 °C for 17 h. The mixture was chromatographed on silica gel (250 g) with toluene/ethyl acetate (70:30). Compound **11** was recovered as a yellow solid in 30% yield: mp, decomposition; ^1H NMR ($CDCl_3$) δ 2.40 (CH_2), 1.97 (CCH_3), 3.70 (CH), 3.80 (OCH_3); ^{31}P NMR ($CDCl_3$) δ 207.15 ($^1J_{PW}$ = 239 Hz); ^{13}C NMR ($CDCl_3$) δ 15.69 (CCH_3), 31.62 (CH_2), 52.16 (OCH_3), 59.13 (CH), 139.34 (:CH), 145.09 (:C–), 164.54 (COO), 195.62 (CO). Anal. Calcd for $C_{36}H_{32}O_{18}P_2W_2$: C, 36.55; H, 2.71; P, 5.24. Found: C, 36.12; H, 2.51; P, 4.98.

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[η^1(P),η^1(P′)-1,2-Bis(methoxyphosphino)ethane]decacarbonylditungsten (12). Complex **11** (1.18 g, 1 mmol) was heated at 150 °C for 5 h in a sealed tube with methanol (5 mL). After evaporation, the residue was chromatographed on silica gel (100 g) with hexane/toluene (1:1). Compound **12** was recovered as an unstable colorless oil that was a mixture of two diastereoisomers (1:1): 18% yield; ^{1}H NMR ($CDCl_3$) δ 2.46 (CH_2), 3.66 ($^3J_{HP}$ = 13,2 Hz, CH_3O), 7.49 ($^1J_{PH}$ = 337.4, $^3J_{HH}$ = 1.7 Hz, HP); ^{31}P NMR ($CDCl_3$) δ 108.1 ($^1J_{PH}$ = 337, $^1J_{PW}$ = 279 Hz, first isomer), 107.8 ($^1J_{PH}$ = 337, $^1J_{PW}$ = 279 Hz, second isomer); mass spectrum (200 °C), *m/e* (relative intensity) 802 (M, 21), 422 (M − $W(CO)_7$, 100).

[η^1(P),η^1(P′)-1,2-Bis(3,4-dimethylphospholyl)ethane]tetracarbonyltungsten (13). A mixture of compound **3** (5 g, 0.02 mol), $W(CO)_6$ (10 g, 0.028 mol), and xylene (100 mL) was heated at 145 °C for 2 h. After evaporation, the residue was chromatographed on silica gel (500 g) with toluene/hexane (1:1). Compound **13** was recovered in 36% yield (toluene): mp, decomposition; ^{1}H NMR ($CDCl_3$) δ 2.12 ($^4J_{HH}$ = 0.7 Hz, CH_3), 1.79 (CH_2), 6.28 ($^2J_{HP}$ = 37.0 Hz, :CH); ^{31}P NMR ($CDCl_3$) δ 39.39 ($^1J_{PW}$ = 203 Hz); ^{13}C NMR ($CDCl_3$) δ 17.60 ($^3J_{CP}$ = 11 Hz, CH_3), 28.78 (CH_2), 128.59 ($^1J_{CP}$ = 40.2 Hz, :CH), 151.76 ($^2J_{CP}$ = 7.3 Hz, :C−), 200.77 (CO); IR (decaline) ν(CO) 2015 (s), 1937 (s), 1925 (s), 1905 (vs) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 546 (M, 55), 490 (M − 2CO, 30), 434 (M − 4CO, 87), 406 (M − 4CO − CH_2CH_2, 95). Anal. Calcd for $C_{18}H_{20}P_2O_4W$: C, 39.58; H, 3.69; P, 11.34. Found: C, 39.26; H, 3.73; P, 11.10.

{η^4(C_4)-[η^1(P),η^1(P′)-1,2-Bis(3,4-dimethylphospholyl)ethane]tetracarbonyltungsten}tetracarbonyltungsten (14). A mixture of compound **3** (5 g, 0.02 mol), $W(CO)_6$ (14 g, 0.04 mol), and toluene (150 mL) was heated at 130 °C for 20 h. After evaporation, the residue was chromatographed on silica gel (500 g) with toluene/hexane (1:1). Compound **13** was first recovered in 10% yield and then compound **14** in 13% yield (toluene): mp, decomposition; ^{1}H NMR ($CDCl_3$) δ 1.02 ($^2J_{HP'}$ = 30.2, $^3J_{HP}$ = 8.6 Hz, CH_2P'), 1.97 ($^2J_{HP}$ = 27.5, $^3J_{HP'}$ = 8.0 Hz, CH_2P), 2.18 ($^4J_{HH}$ = 1.0, $^4J_{HP}$ = 1.2 Hz, :CCH_3), 2.41 (−C′CH_3), 2.54 ($^2J_{HP'}$ = 31.3 Hz, P′C′H), 6.23 ($^2J_{HP}$ = 37.5 Hz, :CH); ^{31}P NMR ($CDCl_3$) δ 51.95 ($^2J_{PP'}$ = 24.4 Hz, P), 22.83 (P′); ^{13}C NMR ($CDCl_3$) δ 13.67 ($^3J_{CP}$ = 6.1 Hz, CH_3), 17.39 ($^3J_{CP}$ = 12.2 Hz, CH_3), 15.57 (J_{CP} = 25.6, J_{CP} = 19.5 Hz, CH_2), 39.07 ($^1J_{CP}$ = 40.2 Hz, −C′H), 42.16 (J_{CP} = 19.5, J_{CP} = 18.3 Hz, CH_2), 90.20 ($^2J_{CP}$ = 6.1 Hz, −C′), 127.59 ($^1J_{CP}$ = 45.1, $^3J_{CP}$ = 2.4 Hz, :CH), 152.79 ($^2J_{CP}$ = 8.5 Hz, :C−), 195.38 ($^2J_{CP}$ = 7.0 Hz, CO), 202.47 ($^2J_{CP}$ = 12.2, $^2J_{CP}$ = 11.0 Hz, CO), 210.65 ($^2J_{CP}$ = 15.9, $^2J_{CP}$ = 9.8 Hz, CO), 217.68 ($^3J_{CP'}$ = 3.7 Hz, CO), 219.98 ($^3J_{CP'}$ = 8.5 Hz, CO); IR (CH_2Cl_2) ν(CO) 2030 (s), 1970 (s), 1945 (m), 1925 (vs), 1875 (m) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 811 (M − CO − 3H, 21), 786 (M − 2CO, 10), 730 (M − 4CO, 21), 702 (M − 5CO, 17), 674 (M − 6CO, 21), 646 (M − 7CO, 100). Anal. Calcd for $C_{22}H_{20}P_2O_8W_2$: C, 31.35; H, 2.37; P, 7.36. Found: C, 31.21; H, 2.51; P, 7.02.

{η^1(P),η^1(P′)-1,2-Bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadien-7-yl]ethane}tetracarbonyltungsten (15). Compound **13** (4 g, 7.3 mmol) and dimethyl acetylenedicarboxylate (4 mL, 33.3 mmol) were heated at 80 °C for 3 h. The mixture was chromatographed on silica gel (250 g) with toluene/ethyl acetate (80:20). Compound **15** was recovered in 66% yield: mp decomposition; ^{1}H NMR (C_6D_6) δ 1.97 (CCH_3), 3.58 (OCH_3), 1.76 (CH_2), 3.60 (CH); ^{31}P NMR (C_6D_6) δ 244.37 ($^1J_{PW}$ = 232 Hz); ^{13}C NMR (C_6D_6) δ 16.24 (CCH_3), 32.17 (CH_2), 52.41 (OCH_3), 60.46 (CH), 139.04 (:CCH_3), 146.37 (:CCO), 165.70 (COO), 200.4 7 (CO), 205.50 (CO); IR (decaline) ν(CO) 2010 (m), 1910 (s), 1895 (s), 1870 (m) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 830 (M, 20). Anal. Calcd for $C_{30}H_{32}P_2O_{12}W$: C, 43.39; H, 3.88; P, 7.46. Found: C, 43.27; H, 4.05; P, 7.64.

[η^1(P),η^1(P′)-1,2-Bis(methoxyphosphino)ethane]tetracarbonyltungsten (17). Complex **15** (1 g, 1.2 mmol) was heated at 150 °C for 5 h in a sealed tube with methanol (5 mL). After evaporation, the residue was chromatographed on silica gel (100 g) with toluene. Compound **17** was recovered as a colorless oil in 40% yield; it was a mixture of two diastereoisomers: ^{1}H NMR (C_6D_6) δ 1.33 (CH_2), 3.02 ($^3J_{HP}$ = 13.4 Hz, OCH_3, first isomer), 3.08 ($^3J_{HP}$ = 13.4 Hz, OCH_3, second isomer), 7.14 ($^1J_{HP}$ = 350 Hz, HP); ^{31}P NMR (C_6D_6) δ 138.35 ($^1J_{PH}$ = 350 Hz, both isomers); ^{13}C NMR (C_6D_6) δ 27.44 (CH_2), 57.92 ($^2J_{CP}$ = 2.4 Hz, OCH_3), 199.81 (CO), 207.10 (CO); IR (decaline) ν(CO) 2025 (s), 1940 (s), 1920 (vs) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 450 (M, 28), 422 (M − CO, 34), 420 (M − CO − 2H, 40), 308 (M − 4CO − 2H − CH_2CH_2, 100). Anal. Calcd for $C_8H_{12}P_2O_6W$: C, 21.35; H, 2.69; P, 13.76. Found: C, 20.84; H, 2.52; P, 13.64.

{η^1(P),η^1(P′)-1,2-Bis[(diethylamino)phosphino]ethane}tetracarbonyltungsten (18). Complex **15** (1.7 g, 2.05 mmol), diethylamine (0.5 mL, 4.8 mmol), and toluene (10 mL) were heated at 130 °C for 2 h in a sealed tube. After evaporation, the residue was chromatographed on silica gel (100 g) with toluene. Compound **18** was recovered as a colorless oil in 55% yield; it was a mixture of two diastereoisomers: ^{1}H NMR (C_6D_6) δ 0.87 ($^3J_{HH}$ = 7.3 Hz, CH_3), 2.89 (NCH_2), 1.33 (PCH_2), 6.42 ($^1J_{HP}$ = 340 Hz, PH); ^{31}P NMR (C_6D_6) δ 67.24 ($^1J_{PW}$ = 243, $^1J_{PH}$ = 340 Hz, first isomer), 65.66 ($^1J_{PW}$ = 243, $^1J_{PH}$ = 340 Hz, second isomer); ^{13}C NMR (C_6D_6) δ 14.84 (CH_3), 27.14 (CH_2P), 45.86 (CH_2N), 201.99 ($^2J_{CP}$ = 7.3 Hz, CO), 203.81 ($^2J_{CP}$ = 9.8 Hz, CO), 207.93 (CO); IR (decaline) ν(CO) 2020 (m), 1925 (m), 1905 (s) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 532 (M, 75), 502 (M − 2H − CO, 36), 474 (M − 2H − 2CO, 25), 446 (M − 2H − 3CO, 83), 418 (M − 2H − 4CO, 36), 390 (M − 2H − 4CO − CH_2CH_2, 100). Anal. Calcd for $C_{14}H_{26}N_2P_2O_4W$: C, 31.58; H, 4.92; N, 5.26; P, 11.65. Found: C, 31.15; H, 4.92; N, 4.83; P, 11.87.

[η^1(P),η^1(P′)-1,2-Bis(2,3-diphenylphosphiren-1-yl)ethane]tetracarbonyltungsten (19). Complex **15** (0.75 g, 0.9 mmol), tolan (0.8 g, 4.5 mmol), and toluene (7 mL) were heated at 130 °C for 2 h in a sealed tube. After evaporation, the residue was chromatographed on silica gel (100 g) with toluene/hexane (1:1). Compound **19** was recovered in 40% yield: mp, decomposition; ^{1}H NMR ($CDCl_3$) δ 1.65 (CH_2), 7.5–8 (Ph); ^{31}P NMR ($CDCl_3$) δ −115.13 ($^1J_{PW}$ = 268 Hz); ^{13}C NMR ($CDCl_3$) δ 31.71 (CH_2), 128.45 (:C), 199.86 (CO); IR (decaline) ν(CO) 2010 (m), 1895 (s), 1870 (s) cm^{-1}; mass spectrum (250 °C) *m/e* (relative intensity) 742 (M, 30), 630 (M − 4CO, 100). Anal. Calcd for $C_{34}H_{24}P_2O_4W$: C, 54.98; H, 3.23; P, 8.35. Found: C, 54.84; H, 3.05; P, 8.37.

[η^1(P),η^1(P′)-1,2-Bis(2-phosphabicyclo[6.1.0]non-2-yl)ethane]tetracarbonyltungsten (20). The same procedure as for **19** was used, with complex **15** (0.75 g, 0.9 mmol) and cyclooctene (0.5 g, 4.5 mmol). Compound **20** was recovered in 68% yield: mp, decomposition; it was a mixture of three isomers; ^{1}H NMR (C_6D_6) δ 0.6–2.3 (CH_2, CH); ^{31}P NMR (C_6D_6) δ −126.27 (first isomer), −133.95 (second isomer), −126.3 ($^2J_{PP}$ = 29.3 Hz), −132.0 (third isomer); ^{13}C NMR (C_6D_6) δ 18.33 (CH), 21.87 − 31.2 (CH_2), 199.68 (CO), 207.5 (CO); IR (decaline) ν(CO) 2015 (m), 1920 (s), 1910 (s), 1895 (s), 1870 (s), 1855 (s) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 606 (M, 25). Anal. Calcd for $C_{22}H_{32}P_2O_4W$: C, 43.58; H, 5.32; P, 10.22. Found: C, 43.69; H, 4.88; P, 10.27.

[η^1(P),η^1(P′)-1,2-Bis(chlorophosphino)ethane]tetracarbonyltungsten (21). A stream of gaseous anhydrous HCl was bubbled for 10 min through a toluene solution of complex **18** (20 mL of toluene, 1.1 g of **18** (2 mmol)) at room temperature. The reaction was complete when the ^{31}P resonance of **18** had disappeared: ^{1}H NMR ($CDCl_3$) δ 2.48 (CH_2), 7.8 ($^1J_{HP}$ = 366 Hz, HP); ^{31}P NMR (C_6D_6) δ 73.33 ($^1J_{PW}$ = 269 Hz); ^{13}C NMR (C_6D_6) δ 31.83 (CH_2), 197.38 (CO), 204.30 (CO); IR ($CDCl_3$) ν(CO) 2040 (m), 1930 (s) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 458 (M, 40), 346 (M − 4CO, 70), 318 (M − 4CO − CH_2CH_2, 100). Anal. Calcd for $C_6H_6Cl_2P_2O_4W$: C, 15.71; H, 1.32; P, 13.50. Found: C, 15.49; H, 1.37; P, 13.54.

[η^1(P),η^1(P′)-1,2-Bis(2,3-diphenylphospiren-1-yl)ethane]diiodotricarbonyltungsten (22). Complex **19** (0.260 g, 0.35 mmole) was treated with I_2 (0.1 g, 0.39 mmol) at room temperature in CH_2Cl_2 (10 mL) for 45 min. Complex **22** crystallized in CH_2Cl_2 and was recovered in 54% yield: mp, decomposition; ^{1}H NMR ($CDCl_3$) δ 2.32 (CH_2), 7.53–8.07 (Ph); ^{31}P NMR ($CDCl_3$) δ −114.38 ($^1J_{PW}$ = 215 Hz); IR (decaline) ν(CO) 2020 (s), 1960 (s), 1895 (s) cm^{-1}. Anal. Calcd for $C_{33}H_{24}I_2O_3P_2W$: C, 40.94; H, 2.50; I, 26.21; P, 6.40; W, 18.99. Found: C, 40.79; H, 2.51; I, 25.84; P, 5.96; W, 18.13.

[η^1(P),η^1(P′)-1,3-Bis(3,4-dimethylphospholyl)propane]tetracarbonyltungsten (23). The same procedure as for **13** was used with compound **4** replacing phosphine **3**. Complex **23** was recovered in 14% yield: mp, decomposition; ^{1}H NMR ($CDCl_3$) δ 2.13 ($^4J_{HH}$ = 0.7 Hz, CH_3), 1.85 (CH_2), 6.42 ($^2J_{HP}$ = 36.2 Hz, :CH);

^{31}P NMR ($CDCl_3$) δ -5.69 ($^1J_{PW}$ = 198 Hz); ^{13}C NMR ($CDCl_3$) δ 17.26 (CH_3), 26.11 (CH_2), 27.44 (PCH_2), 131.16 (:CH), 149.4 (:C-), 201.1 (CO), 204.4 (CO); IR (decaline) ν(CO) 2010 (m), 1905 (m), 1870 (s) cm^{-1}; mass spectrum (250 °C), m/e (relative intensity), 560 (M, 50), 532 (M - CO, 6), 504 (M - 2CO, 20), 476 (M - 3CO, 25), 448 (M - 4CO, 100). Anal. Calcd for $C_{19}H_{22}O_4P_2W$: C, 40.71; H, 3.93; P, 11.07. Found: C, 40.80; H, 4.03; P, 11.10.

{η^1(P),η^1(P')-1,3-Bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadien-7-yl]propane}tetracarbonyltungsten (24). The same procedure as for **15** was used for compound **23**. Compound **24** was recovered in 22% yield: mp, decomposition; ^{1}H NMR (C_6D_6) δ 1.85 (CH_3), 1.23 (CH_2), 1.91 ($^2J_{HP}$ = 1.5 Hz, PCH_2), 3.43 (OCH_3), 3.50 (CH); ^{31}P NMR ($CDCl_3$) δ 216.13 ($^1J_{PW}$ = 225 Hz); ^{13}C NMR ($CDCl_3$) δ 15.75 (CH_3), 19.93 (CCH_2), 33.50 (PCH_2), 52.34 (OCH_3), 60.88 (CH), 138.43 (:CH), 145.28 (:C-), 165.45 (COO), 200.53 ($^2J_{CP}$ = 7.3 Hz, CO), 203.43 (CO); IR (decaline) ν(CO) 2015 (s), 1938 (s), 1903 (s), 1865 (s) cm^{-1}; mass spectrum (250 °C), m/e (relative intensity), 844 (M, 38). Anal. Calcd for $C_{31}H_{34}O_{12}P_2W$: C, 44.07; H, 4.03; P, 7.34. Found: C, 43.85; H, 3.88; P, 7.18.

[η^1(P),η^1(P')-1,3-Bis(2,3-diphenylphosphiren-1-yl)propane]tetracarbonyltungsten (25). The same procedure as for **19** was used for compound **24**. Compound **25** was recovered in 14% yield: mp, decomposition; ^{1}H NMR ($CDCl_3$) δ 1.7-2 (CH_2); ^{31}P NMR ($CDCl_3$) δ -158.0 ($^1J_{PW}$ = 244 Hz); IR (decaline) ν(CO) 2010 (m), 1905 (m), 1890 (m), 1870 (s) cm^{-1}; mass spectrum (250 °C), m/e (relative intensity) 756 (M, 10), 672 (M - 3CO, 25), 644 (M - 4CO, 38). Anal. Calcd for $C_{35}H_{26}O_4P_2W$: C, 55.55; H, 3.44; P, 8.20. Found: C, 55.51; H, 3.37; P, 8.00.

[η^1(P),η^1(P')-1,2-Bis(3,4-dimethylphospholyl)ethane]nickel Dichloride (26). A mixture of compound **3** (1.5 g, 6 mmol) and $NiCl_2$ (0.78 g, 6 mmol) in toluene (10 mL) and EtOH (10 mL) was heated at 70 °C for 3 h. Compound **26** was recovered by crystallization in $CHCl_3$ in 92% yield: mp, decomposition; ^{1}H NMR ($CDCl_3$) δ 2.02 ($^4J_{HH}$ = 0.72 Hz, CH_3), 2.20 (CH_2), 6.48 (:CH); ^{31}P NMR (CD_3OD) δ 67.69; ^{13}C NMR (CD_3OD) δ 18.40 (CH_3), 27.79 (CH_2P), 123.70 (:CH), 155.44 (:C-); mass spectrum (200 °C), m/e (relative intensity) 250 (M - $NiCl_2$, 100). Anal. Calcd for $C_{14}H_{20}Cl_2PNi$: C, 44.33; H, 5.28. Found: C, 44.89; H, 5.53.

Registry No. **2**, 106232-17-1; **3**, 106250-08-2; **4**, 106232-18-2; **5**, 106232-19-3; **6**, 67918-40-5; **8**, 106232-20-6; **9**, 106232-21-7; **10**, 106232-02-4; **11**, 106232-03-5; **12** (isomer 1), 106232-04-6; **12** (isomer 2), 106293-89-4; **13**, 106232-05-7; **14**, 106232-06-8; **15**, 106232-07-9; **17a**, 106293-85-0; **17b**, 106232-16-0; **18a**, 106232-08-0; **18b**, 106293-86-1; **19**, 106232-09-1; **20a**, 106232-10-4; **20b**, 106293-87-2; **20c**, 106293-88-3; **21**, 106232-11-5; **22**, 106232-12-6; **23**, 106250-07-1; **24**, 106232-13-7; **25**, 106232-14-8; **26**, 106232-15-9; Li, 7439-93-2; $ClCH_2Cl$, 75-09-2; $Cl(CH_2)_2Cl$, 107-06-2; $Cl(CH_2)_3Cl$, 142-28-9; $Cl(CH_2)_4Cl$, 110-56-5; S_8, 10544-50-0; $W(CO)_2THF$, 36477-75-5; $W(CO)_6$, 14040-11-0; HCl, 7647-01-0; $(Et)_2NPHCH_2CH_2PHN(Et)_2$, 106232-23-9; 1-phenyl-3,4-dimethylphosphole, 30540-36-4; dimethyl acetylene dicarboxylate, 762-42-5; tolan, 501-65-5; cyclooctene, 931-88-4; 1,2-bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phophanorbornadien-7-yl]ethane, 106232-22-8; methanol, 67-56-1; diethylamine, 109-89-7; 1,3-bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadien-7-yl]propane, 106232-24-0.

(η-Thiophene)Mn(CO)$_3^+$ as a Model for Thiophene Reactivity on Hydrodesulfurization Catalysts

Sara C. Huckett, Nancy N. Sauer, and Robert J. Angelici*

Department of Chemistry and Ames Laboratory,[1] Iowa State University, Ames, Iowa 50011

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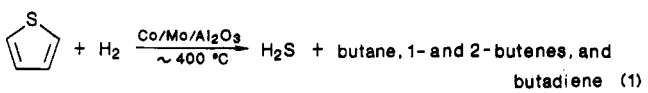
As a model for surface hydride transfer to thiophene π-bonded to a hydrodesulfurization (HDS) catalyst, $HFe(CO)_4^-$ was reacted with (η-thiophene)Mn(CO)$_3^+$ (**1**) to give the product (η^4-thiophene·H)Mn(CO)$_3$ (**3a**) in which H^- added to the 2-position of the thiophene ligand. The analogous reaction with $DFe(CO)_4^-$ shows that D^- adds to both the exo and endo sides of the thiophene ring. The (η-2-methylthiophene)Mn(CO)$_3^+$ complex **4** adds H^- from $HFe(CO)_4^-$ (or BH_4^-) at the non-methylated carbon, C_5, adjacent to the sulfur to give (η^4-2-methylthiophene·H)Mn(CO)$_3$ (**5**). These results are discussed in terms of the observed reactivity of methyl-substituted thiophenes in the HDS process. A hydride (H^-) is abstracted from **3a** and **5** when reacted with Ph_3C^+ to give **1** and **4**, respectively. Deuterium studies show that only the exo H^- (or D^-) is abstracted from **3a**.

Introduction

Hydrodesulfurization (HDS), the catalytic removal of sulfur from crude oil and coal liquids over a sulfided-cobalt-promoted molybdenum catalyst, has been studied extensively because of its widespread commercial use.[2] The HDS reaction of thiophene, an example of an organosulfur compound which is desulfurized with substantial difficulty, is shown in eq 1. Even for thiophene, which has been the subject of numerous investigations, most aspects of the mechanism are still being debated.[3] The initial mode of interaction of thiophene with the catalyst surface as well as the desulfurization pathway are areas which remain unclear.



(1)

Of several proposed binding modes, π-bonding of the aromatic π-system of thiophene with a metal site on the catalyst surface is supported by recent investigations. Benziger et al.[4] examined adsorption and desulfurization of thiophene on clean and sulfided Ni(111) surfaces by using reflection-adsorption infrared spectroscopy (RAIS). Their data suggested that the thiophene ring adsorbs parallel or nearly parallel to the nickel surface at 273 K.

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