The First Free 7λ^3-Phosphanorbornadiene

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Abstract: The first uncoordinated 7λ^3-phosphanorbornadiene **10** is reported. This missing member of the class of 7-heteranorbornadienes was prepared by decomplexation of its pentacarbonyltungsten complex **6** with iodine and *N*-methylimidazole. It is moderately stable at room temperature toward loss of the phosphinidene bridge (PhP:) because the aromatic fragment, [5]metacyclophane (**5**), is a highly strained compound. For this reason, **10** may be considered to be a hyperstable compound. An analysis of the energetics of the system by density functional calculations supports this rationalization.

Introduction

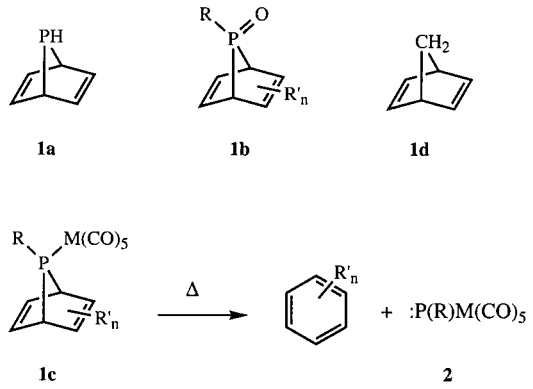
In this study we report the first synthesis of a moderately stable derivative of 7λ^3-phosphanorbornadiene (**1a**) containing trivalent, uncoordinated phosphorus (Scheme 1). Such compounds have, despite considerable effort, so far remained elusive.[1,2] Only two types of stabilized derivatives have been described in which the phosphorus bridge was either oxidized to a phosphine oxide or protected by metal complexation.

Stille and co-workers[2] demonstrated the accessibility of phosphine oxides which are analogues of **1b**, but only if they are stabilized by benzoanellation.[3,4] However, all attempts to reduce their P═O bond proved futile, presumably because the reduced compounds rapidly extrude the phosphorus bridge.[2]

So far, the only stable derivatives of **1a** have been the *complexes* **1c**, prepared by Mathey and Marietti in 1982,[5] in which phosphorus is coordinated to $Cr(CO)_5$, $Mo(CO)_5$, or $W(CO)_5$ (Scheme 1). At temperatures around 100 °C, these decompose by cheletropic elimination to give a substituted benzene and a transient terminal complexed phosphinidene $:P(R)M(CO)_5$ (**2**), which behaves as a versatile carbene-like synthon.[5]

The failure to obtain (a derivative of) **1a** with a free trivalent phosphorus is all the more peculiar against the background that many 7-heteranorbornadienes are known which contain elements of Groups 14−16 in the bridge position. Their stability depends critically on the tendency for cheletropic elimination of the hetero-bridge to give a stable aromatic fragment. This tendency increases for the heavier elements, presumably due to the decreasing element−carbon bond strength and the increasing stability of the divalent hetero-fragment.

Scheme 1[a]



[a] M = Cr, Mo, W.

In Group 14, the parent norbornadiene (**1d**) is thermally rather stable. In contrast, 7-norbornadienone (**1e**) decarbonylates above −30 °C to give benzene and CO, for which a synchronous concerted pathway was proposed based on the low activation energy of 63 ± 10 kJ mol^{-1} (Scheme 2).[6] Such elimination reactions have even been exploited for the synthesis of unstable and unusual molecules. Thus, the fragmentation of 7-norbornadieneazine (**1f**) furnished, besides benzene, the two highly unstable C_2N_2 isomers of cyanogen, isocyanogen (**3**),[7] and diisocyanogen (**4**).[8]

7-Silanorbornadienes **1g**, first prepared by Gilman and coworkers in 1964,[9] decompose above 250 °C with loss of the silylene bridge (Scheme 3), possibly via a radical mechanism.[10]

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(4) Matsumoto, K,; Hashimoto, S.; Otani, S.; Uchida, T. *Heterocycles* **1984**, *22*, 2713.
(5) (a) Marinetti, A.; Mathey, F.; Fischer, F.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667. (b) Marinetti, A.; Mathey, F.; Fischer, F.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 4484. (c) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488. (d) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, F. *Organometallics* **1985**, *4*, 2134. (e) For a review see: Mathey, F. *Angew. Chem.* **1987**, *97*, 285; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275.
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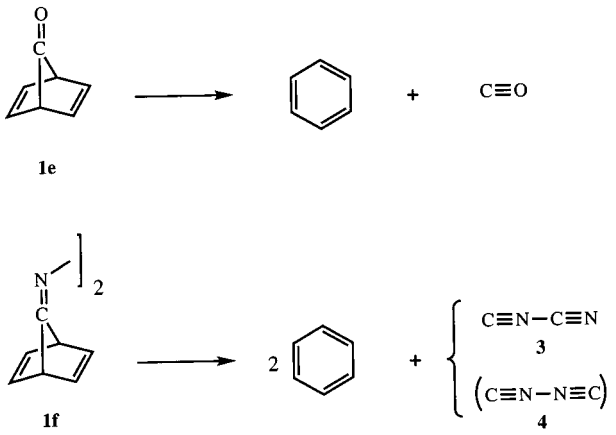
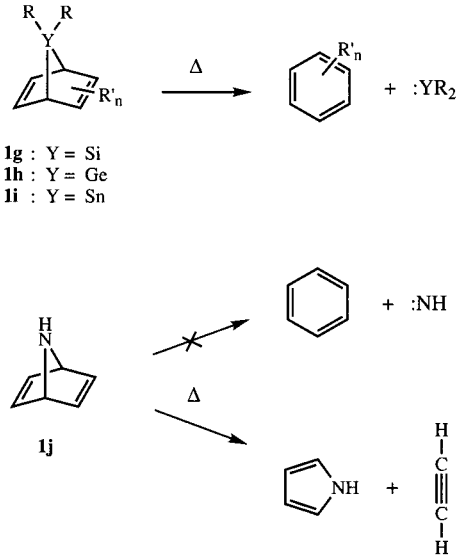
Scheme 2



Scheme 3[a]



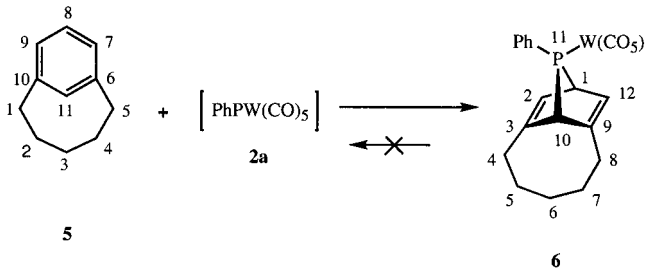
[a] MeIm = *N*-methylimidazol.

Likewise, 7-germanorbornadienes **1h** extrude germylenes already around 150 °C.[11] This trend of decreasing stability for the heavier elements continues for 7-stannanorbornadienes **1i** which have not been isolated yet as they decompose on attempted synthesis.[12]

7-Heteranorbornadienes of Group 16 are accessible by Diels−Alder reactions of alkynes with furan[13] and thiophene.[14] The heavier analogues with the 7-thia bridge are too unstable to survive the (drastic) conditions required for their formation.

So far, only the nitrogen derivatives were known from the Group 15 7-heteranorbornadienes.[15] The parent system **1j** was prepared in 1982 by Vogel and co-workers. Above 80 °C, **1j** fragments, but *not* by the usual elimination of the bridging nitrene :NH; instead, a retro-Diels−Alder reaction furnishes pyrrole and acetylene (Scheme 3).[15j] Again, the higher analogues of Group 15 with a PR bridge proved to be too unstable for isolation.[1,2]

Scheme 4



Results and Discussion

Synthesis of 10. In pursuit of an *uncomplexed* 7-phosphanorbornadiene, it occurred to us that the tremendous driving force for cheletropic elimination of the phosphorus bridge can be diminished by destabilizing the second fragment, the aromatic compound. This may be accomplished by incorporation of strain in the latter, e.g. by bending the aromatic ring as in small cyclophanes.[16] Recently, we reported the synthesis of the transition metal complexed 7-phosphanorbornadiene **6** by the unprecedented 1,4-addition of $PhPW(CO)_5$ (**2a**) to the highly bent [5]metacyclophane (**5**) (Scheme 4).[17] The extraordinary thermal stability of **6** was explained by the unfavorable thermodynamics for the retro reaction as the strain in **5** is much higher than that in **6**. We therefore envisioned **6** to be a promising candidate for generating the elusive uncomplexed 7-phosphanorbornadiene system.

For this purpose, we applied a decomplexation method reported by Mathey and co-workers for the preparation of phosphirenes from the corresponding complexes.[18] In this approach, the P−W bond is weakened and finally cleaved by first oxidizing W(0) to W(II) with iodine, followed by exchange of the CO ligands with *N*-methylimidazole (MeIm).

Monitoring the addition of 1 equiv of I_2 to a solution of **6** in CD_2Cl_2 at −30 °C by ^{31}P NMR spectroscopy showed two new resonances at 153.4 and 148.0 ppm to emerge in a 3:2 ratio which are tentatively assigned to two stereoisomers of the W(II) complex **7** (Scheme 5). These isomers exchange slowly as indicated by broadening of the signals on warming, with coalescence occurring at room temperature. The reduced

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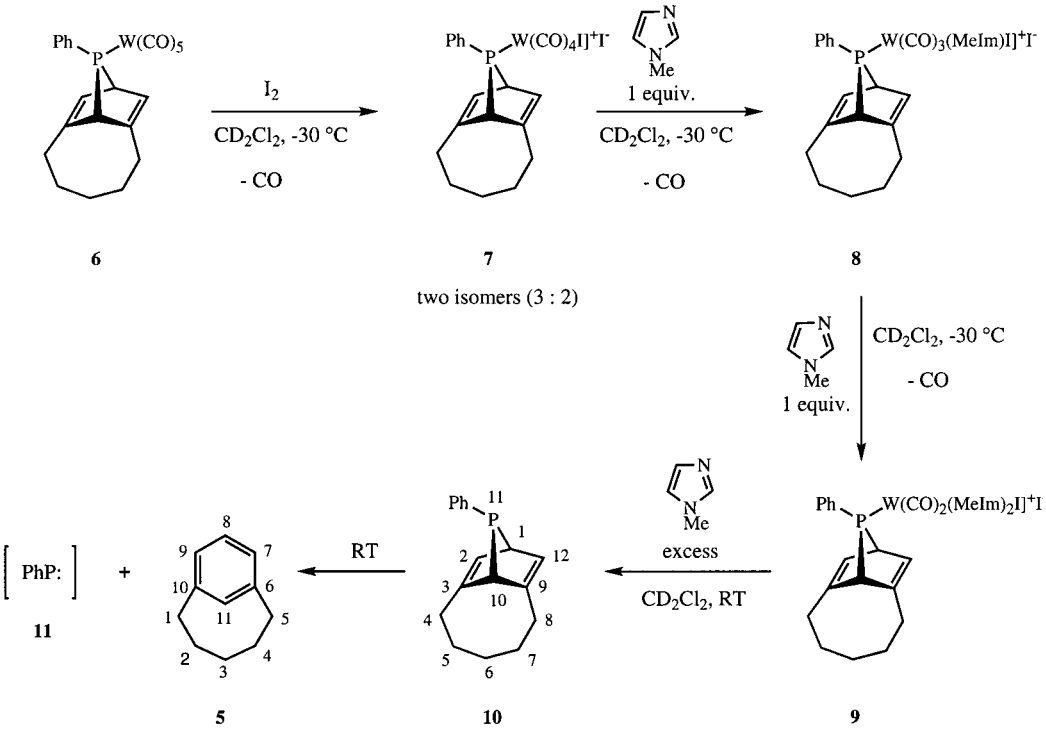
Scheme 5



coupling constants of **7** (major isomer: ^1J (P,W) = 142 Hz) as compared to that of **6** (^1J (P,W) = 227 Hz) may signal a weakened P−W bond.

To accomplish a stepwise exchange of the metal ligands of **7**, we first added 1 equiv of MeIm at −30 °C. The resulting new ^{31}P NMR resonance at 179.5 ppm (^1J(P,W) = 172 Hz) is tentatively assigned to **8**. On addition of a second equivalent of MeIm at −30 °C, **8** was converted to a new compound, presumably **9** (δ(^{31}P) = 173.5 ppm, ^1J(P,W) = 127 Hz), which is extremely air sensitive, but stable at room temperature under inert conditions. Only upon addition of a third equivalent of MeIm did a slow decomposition take place (at 298 K, first-order kinetics with a half-life time of 6 h) under formation of a new organophosphorus compound having a ^{31}P NMR resonance at 112 ppm without P,W coupling. To this compound, we assign the structure of the uncomplexed 7λ^3-phosphanorbornadiene **10**.

Characterization of 10. Attempts to isolate **10** were unsuccessful because it decomposes at room temperature and did not survive attempted chromatographic purification. However, its structure was corroborated by NMR spectroscopy and by direct inlet HR-MS.

The phosphorus nucleus of **10** is strongly deshielded for a tertiary phosphine, but similar shifts in the range of 60−150 ppm have been reported for related 7-phosphanorbornenes.[19] A theoretical study[20] attributed this deshielding to anisotropy effects and predicted that incorporation of a second double bond, as in the corresponding 7-phosphanorbornadiene, would cause stronger shielding of the phosphorus. However, in the present case we find this effect on the chemical shift to be small.

The identity of **10** is further supported by its ^{1}H and ^{13}C NMR spectra, which are closely related to those of its W(CO)$_5$ complex **6**.[17] Indicative are the olefinic protons, which appear as two doublets at 6.20 and 5.87 ppm. The bridgehead carbons C1 and C10 resonate at 57.60 and 50.16 ppm, respectively. Whereas their coupling constants ^1J(C,P) = 62.1 and 52.4 Hz confirm an intact norbornadiene structure, they are strikingly different from those of **6** (^1J(C,P) = 26.2 and 20.2 Hz). An analogous increase of ^1J(C,P) on decomplexation is found in the couple (pentacarbonyltungsten)phosphirane ([C$_2$H$_4$PH]W(CO)$_5$, ^1J(C,P) = 10.4 Hz[21]) and phosphirane (C$_2$H$_4$PH:, ^1J(C,P) = 33 Hz[22]).[23]

At room temperature, **10** slowly fragments (half-life time of about 1 day) into [5]metacyclophane (**5**) and presumably phenylphosphinidene (**11**), which, however, did not form products detectable by ^{31}P NMR spectroscopy. The recovery of **5** was estimated at 80%, based on the appearance of its characteristic ^{1}H NMR resonance at 0.25 ppm. Attempted analysis by GCMS revealed that under these conditions, **10** is also completely converted to **5** as the sole detectable product.

Calculational Analysis. We were struck by the ease of formation of **5** in view of its high strain energy of 174 kJ mol^{-1} (DFT)[24] and because 7-azanorbornadienes disproportionate by a different pathway yielding pyrroles and alkynes (cf. **1j**, Scheme 3).[15j] We therefore applied density functional calculations (B3LYP/6-31G*[25]) to distinguish between the two decomposition modes for the parent systems **1j** and **1a**, namely either by a retro cycloaddition giving the five-membered heterocycles [pyrrole (**12j**) and phosphole (**12a**), respectively] together with acetylene (Scheme 6, pathway a) or by a chelotropic elimination of the bridge [as singlet nitrene (**13**) or phosphinidene (**14**), respectively] furnishing benzene as the second fragment (pathway b).

Pathway a is strongly favored for the 7-azanorbornadiene **1j** (ΔH^{298}(a) = +1.0 kJ mol^{-1}, ΔH^{298}(b) = +237 kJ mol^{-1}), in agreement with experimental observations.[15j] In contrast, the

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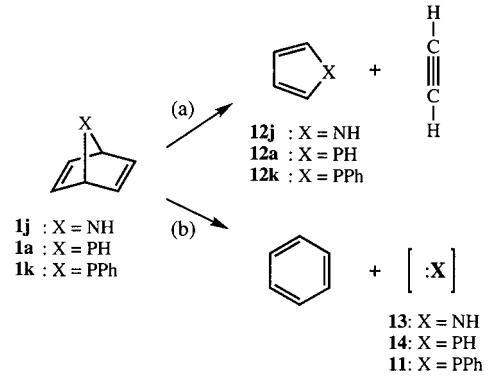
Scheme 6



7-phosphanorbornadiene **1a** slightly favors pathway b, i.e., the elimination of phosphinidene (**14**) (ΔH^{298}(a) = +113 kJ mol^{-1}, ΔH^{298}(b) = +108 kJ mol^{-1}). This preference becomes more pronounced on phenyl substitution at phosphorus (**1k**) as it stabilizes the resulting phenylphosphinidine (**11**) considerably (ΔH^{298}(a) = +112 kJ mol^{-1}, ΔH^{298}(b) = +42 kJ mol^{-1}).[26] It is clear that the elimination of a phosphinidene is the preferred reaction channel for a 7-phosphanorbornadiene, in accordance with our experimental observation.

While a comprehensive analysis of the different reaction channels available to **10** was beyond our resources, the computed enthalpy for dissociation into **5** and **11** amounts to ΔH^{298}(b) = +201 kJ mol^{-1}. The impressive difference of $\Delta\Delta H^{298}$(b) = +159 kJ mol^{-1} for the fragmentations of **10** and **1k** largely reflects the strain in [5]metacyclophane **5** (ΔH(SE)= 174 kJ mol^{-1}),[24] and explains the stability of **10** relative to that of "normal" derivatives of **1a** that do not contain a pentamethylene bridge.

Finally, we note that the calculated structure of **10** (Figure 1) closely resembles the X-ray crystal structure of **6**.[17] Decomplexation has only a minor influence on the 7-phosphanorbornadiene skeleton. The differences between **10** and the unbridged analogue **1k** (Figure 2) are more striking. For example, the C1−P bond of **10** (1.913 Å) is shorter than that of **1k** (1.941 Å), reflecting a tighter binding of the phosphorus bridge. Also in contrast to **1k**, but similar to the W(CO)$_5$ complex **6**,[17] the double bonds in **10** are strongly twisted (−165.8° [C1−C2−C3−C4] and 167.6(4)° [C8−C9−C12−C1]). This, together with the large C−C−C angles in the pentamethylene bridge (118.0−118.8°), signals a significant degree of strain in **10**, though much less than that in **5**.

Conclusion

The first free 7λ³-phosphanorbornadiene derivative **10** has been prepared by decomplexation of its pentacarbonyltungsten complex **6**. On one hand, the propensity of **10** toward elimination of the bridging group is in line with the trend observed for other 7-heteranorbornadienes with heavier elements in the bridge. On the other hand, its stability at room temperature, be it only moderate, is remarkable because all previous attempts to obtain a simple, unbridged 7λ³-phosphanorbornadiene had failed.

Obviously, **10** owes its kinetic stabilization to the overall increase in strain that results on dissociation. Normally, the stability of the aromatic fragment is the thermodynamic driving force for the fragmentation process. In the present case, the considerable energy content of the highly strained aromatic fragment, [5]metacyclophane (**5**), reduces the rate of this

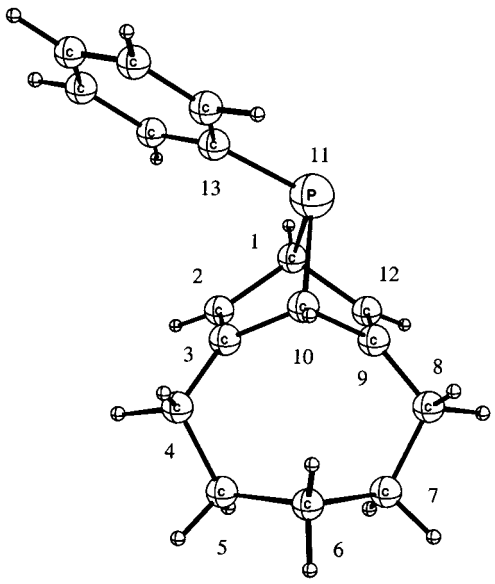


Figure 1. Calculated structure of **10**. Selected bond lengths [Å] and angles [deg]: P11−C13 1.853, P11−C1 1.913, P11−C10 1.919, C1−C2 1.535, C1−C12 1.540, C2−C3 1.340, C3−C10 1.529, C9−C12 1.344, C9−C10 1.534; C13−P11−C1 106.7, C13−P11−C10 105.8, C1−P11−C10 76.9, C2−C1−C12 107.2, C2−C1−P11 103.8, C12−C1−P11 94.6, C3−C2−C1 110.5, C2−C3−C10 109.2, C12−C9−C10 109.0, C9−C10−C3 106.0, C9−C10−P11 96.1, C3−C10−P11 105.1, C9−C12−C1 110.5, C3−C4−C5 113.6, C4−C5−C6 118.8, C5−C6−C7 118.0, C6−C7−C8 118.8, C7−C8−C9 113.2; C1−C2−C3−C4 165.8, C8−C9−C12−C1 167.6.

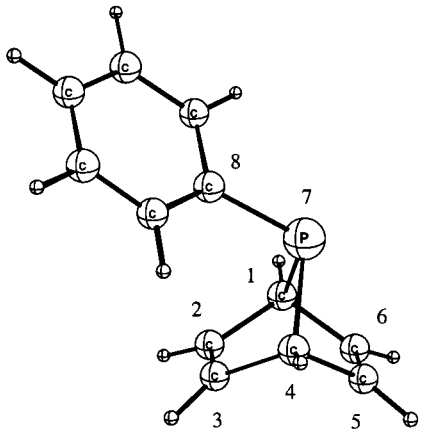


Figure 2. Calculated structure of **1k**. Selected bond lengths [Å] and angles [deg]: P7−C8 1.852, P7−C1 1.941, P7−C4 1.925, C1−C2 1.526, C1−C6 1.532, C2−C3 1.336, C3−C4 1.531, C4−C5 1.535, C5−C6 1.340; C8−P7−C1 106.4, C8−P7−C4 106.5, C1−P7−C4 76.9, C2−C1−C6 108.5, C2−C1−P7 103.1, C6−C1−P7 93.9, C1−C2−C3 110.5, C2−C3−C4 110.3, C3−C4−C5 108.3, C4−C5−C6 110.3, C3−C4−P7 103.4, C5−C4−P7 94.1, C5−C6−C1 110.3.

(25) All B3LYP/6-31G* calculations were performed with the Gaussian 98 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1998.

(26) Note that these reaction enthalpies do not take into account stabilization in the condensed phase, which should further reduce the endothermicities for elimination of the high energy species nitrene and phosphinidene.

fragmentation. In this respect, **10** can be considered to be a hyperstable derivative.

We feel that the strategy applied for the preparation of **10**, i.e., making the 7-heteranorbornadiene skeleton hyperstable through bridging of the 2- and 6-positions by a short (oligomethylene) chain, will give access to other hitherto unknown representatives of this class, notably those of sulfur and tin.

Experimental Section

Tetracarbonyliodo[11-phenyl-11-phosphatricyclo[7.2.1.0^{3,10}]dodeca-2,9(12)-diene]tungsten Iodide (7). Under nitrogen a solution of **6**[17] (28.9 mg, 0.050 mmol) in CD_2Cl_2 (400 μL) was prepared in a 5 mm NMR tube. After the mixture was cooled to −30 °C, a solution of I_2 (12.7 mg) in 200 mL of CD_2Cl_2 was added. The NMR tube was capped with a Teflon cap and slowly warmed to room temperature. At this point, the extrusion of CO was indicated by gas evolution. After the evolution of CO had ceased, NMR spectra of the solution were recorded at −30 °C. ^{31}P NMR (162.0 MHz, CD_2Cl_2, 243 K): δ 153.4 (^1J(P,W) = 142 Hz), major isomer (59.4%); δ 148.0 (the signal was too broad to determine ^1J(P,W)), minor isomer (41.6%). ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.43−7.18 (m, 5H), 6.33 (dd, ^3J(H,P) = 6.3 Hz, ^3J(H,H) = 4.0 Hz; H12), 6.02 (dd, ^3J(H,P) = 4.2 Hz, ^3J(H,H) = 4.2 Hz; H2), 4.25 (bs; H1), 3.93 (bs; H10), 2.80−0.80 (m; 10H).

Tricarbonyliodo(*N*-methylimidazole)[11-phenyl-11-phosphatricyclo-[7.2.1.0^{3,10}]dodeca-2,9(12)-diene]tungsten Iodide (8). To an NMR tube containing a solution of **7** (vide supra) in CD_2Cl_2 (600 μL) was added under nitrogen at − 30 °C a solution of *N*-methylimidazole (4.1 mg, 0.050 mmol) in CD_2Cl_2 (50 μL). The solution immediately changed color from deep orange to pale yellow. ^{31}P NMR (162.0 MHz, CD_2Cl_2, 243 K): δ 179.5 (^1J(P,W) = 172 Hz).

Dicarbonyliodobis(*N*-methylimidazole)[11-phenyl-11-phosphatricyclo[7.2.1.0^{3,10}]dodeca-2,9(12)-diene]tungsten Iodide (9). To an NMR tube containing a solution of **8** (vide supra) in CD_2Cl_2 (650 μL) was added under nitrogen at − 30 °C a solution of *N*-methylimidazole (4.1 mg, 0.050 mmol) in CD_2Cl_2 (50 μL). The tube was tightly capped with a Teflon cap and transferred to the NMR probe. Unfortunately some signals in the ^{13}C NMR spectrum of **9** were obscured by impurities. Therefore, only those signals which could be assigned with certainty and which are of essence for the identity of **9** are listed. ^{31}P NMR (162.0 MHz, CD_2Cl_2, 298 K): δ 173.6 (^1J(P,W) = 127 Hz). ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 8.25 (bs; 2H), 7.64 (s; 2H), 7.56 (s; 2H), 7.17−7.09 (m; 4H), 6.88 (dd, ^3J(H,P) = 20.8 Hz, ^3J(H,H) = 4.2 Hz; *o*-Ar), 6.20 (dd, ^3J(H,P) = 11.1 Hz, ^3J(H,H) = 4.1 Hz; H12), 6.01 (dd, ^3J(H,P) = 8.6 Hz, ^3J(H,H) = 4.0 Hz; H2), 4.25 (m; H1), 4.07 (bs; H10), 3.79 (s, 6H), 3.10−0.75 (m; 10H). ^{13}C{^{1}H} NMR (100.64 MHz, CD_2Cl_2, 298 K): δ 203.2 (s; CO), 198.3 (s; CO), 158.2 (d, ^2J(C,P) = 10.2 Hz; C3), 156.2 (d, ^2J(C,P) = 19.4 Hz; C9), 61.60 (d, ^1J(C,P) = 34.2 Hz; C1), 52.10 (d, ^1J(C,P) = 25.9 Hz; C10), 37.49 (s; CH_3), 37.00 (s; CH_3), 35.55 (s; CH_2), 35.47 (s; CH_2), 35.44 (s; CH_2), 34.77 (s; CH_2), 26.50 (s; C6).

11-Phenyl-11-phosphatricyclo[7.2.1.0^{3,10}]dodeca-2,9(12)-diene (10). To an NMR tube containing a solution of **9** (vide supra) in CD_2Cl_2 (700 μL) was added under nitrogen at room temperature *N*-methylimidazole (16.4 mg, 0.20 mmol). The tube was tightly capped with a Teflon cap and the decomposition of **9** was monitored by ^{31}P NMR spectroscopy. The complexity of the reaction mixture prevented the complete identification of all resonances of **10**. The most revealing signals are listed below. ^{31}P NMR (162.0 MHz, CD_2Cl_2, 298 K): δ 112.5. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 6.20 (dd, ^3J(H,P) = 12.7 Hz, ^3J(H,H) = 4.4 Hz; H12), 5.87 (dd, ^3J(H,P) = 13.0 Hz, ^3J(H,H) = 4.6 Hz; H2). ^{13}C{^{1}H} NMR (100.64 MHz, CD_2Cl_2, 298 K): δ 57.60 (d, ^1J(C,P) = 62.1 Hz; C1), 50.16 (d, ^1J(C,P) = 52.4 Hz; C10); MS-DI (70 eV) *m*/*z* (%): 256 (variable, only at higher pressures) [M + 2)$^+$), 254 (3.8) [M$^+$], 252 (8.4), 250 (4.4), 236 (27.0), 234 (34.9), 173 (77.0), 155 (100), 153 (57.1), 141 (17.1), 128 (37.3), 115 (52.4), 91 (30.2), 82 (94.9), 77 (35.7), 58 (65.1); HR-MS (direct inlet) $C_{19}H_{19}P$ (*M*$^+$) Calcd.: *m*/*z* 254.1224. Found: 254.1231 ± 0.0009. Due to the instability of **10** at room temperature, an elemental analysis was not obtained.

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