2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene as an η^6-Ligand in Transition Metal Complexes

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Keywords: 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene / η^6-Triphosphabenzene transition metal complexes / Displacement reactions / Phosphorus heterocycles / Arene complexes

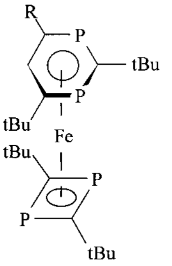
The η^6-1,3,5-triphosphabenzene transition metal complexes **12a**,**b**, **14**, and **16** have been synthesized for the first time by the displacement of η^6-arene ligands (toluene, benzene and naphthalene) with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**9**). The new complexes have been fully characterized by a combination of elemental analysis, mass spectrometry, and ^1H-, ^{13}C- and ^{31}P-NMR spectroscopy.

The discovery of transition metal complexes bearing η^6-benzene ligands has been one of the landmarks in the development of modern organometallic chemistry.[1] Numerous π-arene complexes have since been synthesized,[2] not only containing purely carbon-aromatic systems, but arenes incorporating one or more heteroatoms such as N,[3] P,[4] As or Sb[5] as well. With these heteroarenes, a complication that often arises is that η^1-coordination of the lone pair of the heteroatom is more stable than η^6-coordination to a transition metal.[3−5] With phosphorus as the heteroatom, the preferred bonding mode is η^1-coordination; e.g. at room temperature $M(CO_5)THF$ complexes (M = Cr, Mo, W) react with phosphabenzenes (phosphinines) bearing practically any substituents to give the corresponding pentacarbonyl(η^1-phosphinine)metal complexes.[4][6] Only bulky substituents such as *tert*-butyl groups in the 2,6-positions prevent such an interaction.

η^6-Phosphinine complexes of these metals $[(\eta^6\text{-}C_5R_5P)M(CO)_3]$ can be prepared either from the η^1-complexes by heating above 130 °C or directly from phosphinine and $M(CO)_6$ at 130−150 °C.[4,7a,7b] Displacement of a benzene derivative by a phosphinine represents a further possible synthetic path for preparing e.g. $[(\eta^6\text{-}C_5Ph_3H_2P)Mo(CO)_3]$.[7c]

In contrast to phosphinine complexes, only two examples are known in which 1,3-diphosphabenzene[8] and 1,3,5-triphosphabenzene[9] are η^6-bonded to a transition metal atom. In both cases the complexes are prepared by cyclotrimerization of *tert*-butylphosphaacetylene (**8**) or by cotrimerization of two equivalents of **8** with an acetylene within the coordination sphere of a metal. An earlier report in which the synthesis of the [η^6-triphosphabenzene]molybdenum complex **3** was claimed[10] is dubious for some reason (see below).[11][12]

The binding mode of a cyclic $(PC-tBu)_3$ unit to a transition metal atom appears to be very flexible, depending on the transition metal and on the other ligands connected to



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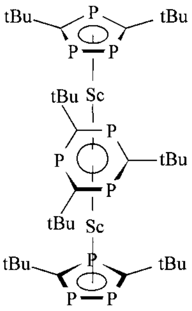

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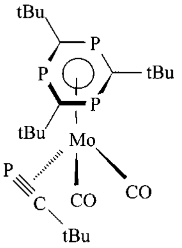

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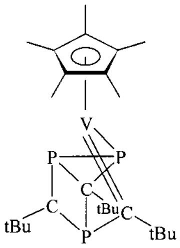
the metal atom. This observation is illustrated by the two vanadium complexes **4** and **5**[13] and the two hafnium complexes **6**[14b,16] and **7**.[14a]



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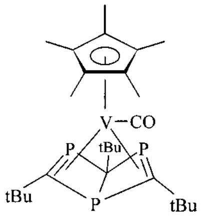

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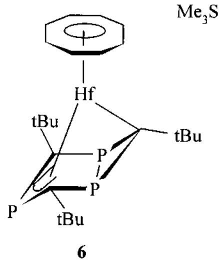

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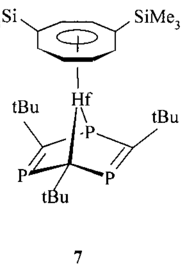

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Complexes **6** and **7**, which are synthesized from *tert*-butylphosphaacetylene (**8**) and (η^4-butadiene)(η^8-cyclooctatetraene)hafnium or the corresponding [1,4-bis(trimethylsi-

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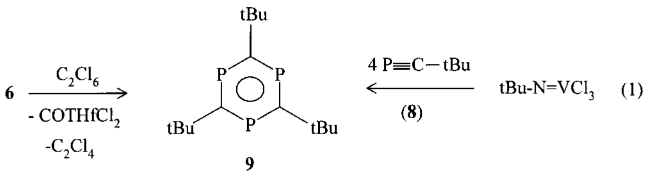
lyl)cyclooctatetraene]hafnium complex, are the starting materials for the preparation of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**9**) and 2,4,6-tri-*tert*-butyl-1,3,5-triphospha Dewar benzene (**10**), respectively, by reaction with hexachloroethane.[14a] For the synthesis of the triphosphabenzene **9**, a direct route has recently been developed, starting from **8** and trichlorovanadium *tert*-butylimide.[15]



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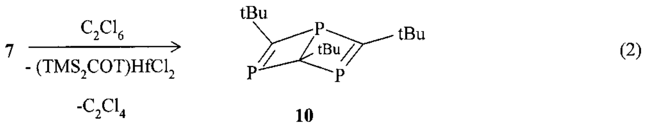


(2)

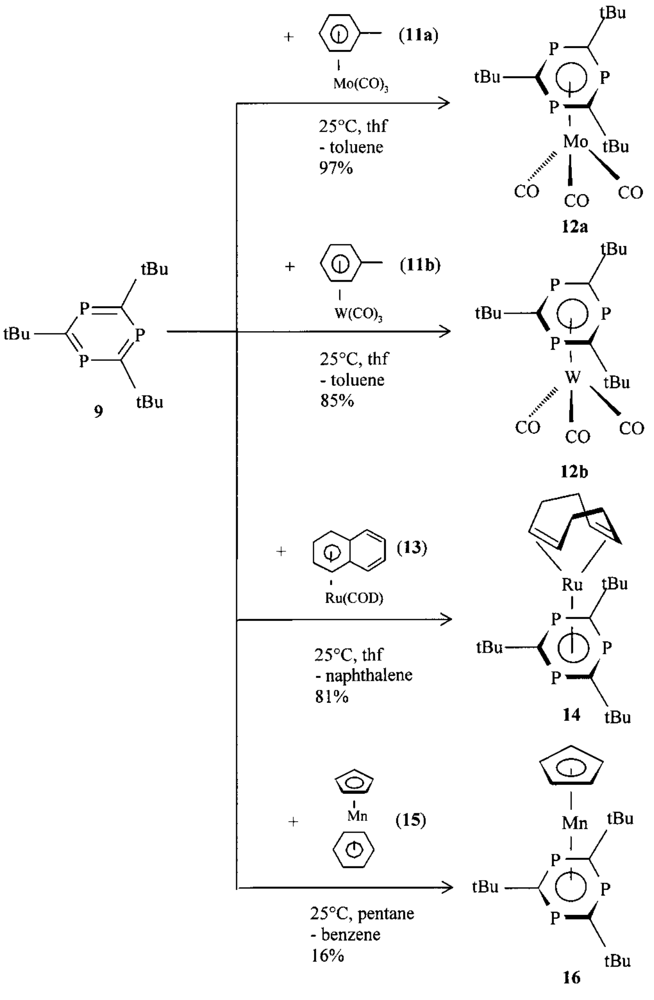
With these procedures at hand, we were able to study the reactivity of the two new heterocycles **9**[16] and **10**.[17][18] Herein we describe the synthesis of some η^6-triphosphabenzene transition metal complexes (M = Mo, W, Ru, Mn) by the displacement of η^6-bonded aromatic ligands (benzene, toluene, naphthalene).

Reactions of tricarbonyl(η^6-toluene)molybdenum (**11a**) and tricarbonyl(η^6-toluene)tungsten (**11b**) with triphosphabenzene **9** in equimolar amounts at ambient temperature result in the displacement of toluene, yielding the molybdenum and tungsten complexes **12a** and **12b** almost quantitatively. This indicates that triphosphabenzene **9** bonds more strongly to the $Mo(CO)_3$ and $W(CO)_3$ fragments than toluene. A primary interaction between one of the lone pairs of the phosphorus atoms in **9** and the metal atom is not observed. Such coordination may be prevented by the bulkiness of the two *tert*-butyl groups in the neighbourhood of the phosphorus atoms. This may also account for the fact that it is not possible to displace nitrile or carbon monoxide from $(RCN)_3M(CO)_3$, $M(CO)_6$, or $(CO)_5M(THF)$ (M = Cr, Mo, W) by **9**. It is known that 2,6-di-*tert*-butylphosphinine does not interact with transition metals via the lone pair either.[19]

The product complexes were isolated as small orange needles (**12a**) and as an orange powder (**12b**). We have so far been unable to obtain crystals suitable for an X-ray analysis. Both complexes decompose above 100°C before reaching their melting point. It is interesting to note that it was not possible to prepare tricarbonyl(η^6-triphosphabenzene)chromium in the same manner from tricarbonyl(η^6-toluene)chromium and **9**.

For the preparation of a (η^6-triphosphabenzene)ruthenium complex, (η^4-1,5-cyclooctadiene)(η^6-naphthalene)ruthenium (**13**) is an ideal starting material. Thus, reaction with the triphosphabenzene **9** leads to substitution of the naphthalene and the new (η^4-1,5-cyclooctadiene)(η^6-triphosphabenzene)ruthenium complex **14** is formed in 81% yield as an orange powder. The product was found to decompose at 105°C.

The displacement of benzene from (η^6-benzene)(η^5-cyclopentadiene)manganese (**15**) by **9** does not reach completion. The reaction proceeds at ambient temperature in pentane only until a conversion of ca. 20% is attained. After separation of the displaced benzene, the reaction does not recommence, thus excluding the possibility of an equilibrium situation. On chromatographic work-up of the reaction mixture, ca. 80% of the starting material **15** can be recovered. Remaining **9** was detected in the distillate and the resulting complex **16** was isolated as green oil in 16% yield.



Scheme 1. Synthesis of some (η^6-triphosphabenzene)metal complexes

All of the new η^6-triphosphabenzene complexes **12a**,**b**, **14**, and **16** have been characterized by elemental analysis, mass spectrometry, and NMR spectroscopy. Elemental analytical data confirm the correct compositions, which are further corroborated by the mass spectra. The molecular ion peak is seen in the mass spectrum of each complex. The $(C_3P_3tBu_3)M$ ions give rise to characteristic fragment ion peaks in the spectra of complexes **12a**, **12b**, and **14**, while in the mass spectrum of the manganese complex **16** the ion of triphosphabenzene **9** and fragmentation ions therefrom are prominent.

The NMR spectra provide the most diagnostic information as to the constitutions of **12a**,**b**, **14**, and **16**. All spectra exhibit the characteristic feature indicative to the free triphosphabenzene ligand **9**, i.e. the three phosphorus atoms, the three ring carbon atoms, and the hydrogen atoms of the *tert*-butyl groups each appear as single signals, indicating a delocalized 6-π-electron system. The η^6-coordination is indicated by upfield shifts, which do not vary much for the ^{13}C-NMR signals ($\Delta\delta = 84.8 - 77.8$, see Table 1), whereas the ^{31}P-NMR shifts are more sensitive to the metal and to the other ligands linked to the metal atom. The coupling pattern of the carbon atoms in free triphosphabenzene **9** ($A_2A'X$) is maintained when **9** is η^6-coordinated to a metal atom. In addition, W−C coupling is observed in the spectrum of **12b**. The carbon atoms of the CO groups in **12a** and **12b** also show coupling with the metal atom and with the three phosphorus atoms of **9**.

Table 1. ^{31}P- and ^{13}C-NMR data of triphosphabenzene as an η^6-ligand in metal complexes in comparison with free triphosphabenzene **9** (δ in ppm)

Compound	9	12a	12b	14	16
M	−	Mo	W	Ru	Mn
P[a]	232.6	57.6	38.6	59.0	−4.7
C[b]	211.8	131.8	127.0	132.6	134.0

[a] Singlet. − [b] $A^2A'X$ system.

The electronically and coordinatively saturated η^6-triphosphabenzene complexes **12a**,**b**, **14**, and **16** are thermally stable up to ca. 100°C and are rather unreactive. Thus, it was found that the ruthenium complex **14** may be used as a catalyst for the hydrogenation of 1-hexene (THF, 20°C, 20 bar H_2, 0.5 mol-%, 90 h), although the hydrogenation rate is nine times slower than that observed using (η^6-benzene)(1,5-cyclooctadiene)ruthenium as catalyst under comparable conditions.[20][21] Complex **12a** does not react with **9** under the conditions under which Cowley et al.[9] claimed to have synthesized the first η^6-triphosphabenzene complex **3** (THF, 65°C, 10 h). This result, together with the observation of Scheer et al.,[12] led us to the conclusion that Cowley et al. did not in fact synthesize complex **3**. Therefore, the complexes **12a**,**b**, **14**, and **16** can be regarded as the first unambiguously characterized mononuclear metal complexes bearing a triphosphabenzene as an η^6-coordinated ligand.

Experimental Section

All experiments were carried out under argon in anhydrous solvents. − MS: Finnigan MAT 311 ADF, 70 eV. − ^{1}H and ^{13}C NMR: Bruker AM 200 and AMX 400; chemical shifts measured relative to solvent, numerically relative to TMS. − ^{31}P NMR: Bruker AM 200 and AMX 400; external standard H_3PO_4. − Elemental analyses: Dornis and Kolbe, Mülheim a. d. Ruhr. − 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene (**9**),[14a,15] tricarbonyl(η^6-toluene)molybdenum (**11a**) and tricarbonyl(η^6-toluene)tungsten (**11b**),[22] (η^4-cyclooctadiene)(η^6-naphthalene)ruthenium (**13**),[23] and (η^6-benzene)(η^4-cyclooctadiene)manganese (**15**)[24] were prepared according to published procedures.

Tricarbonyl(η^6-2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene)-molybdenum (12a): To a solution of tricarbonyl(η^6-toluene)molybdenum (**11a**, 0.5 g, 1.8 mmol) in THF (10 mL), **9** (0.54 g, 1.8 mmol) was added at room temperature. After stirring for 4 h, the solution was concentrated to a volume of 3 mL and then cooled to −78°C. Complex **12a** precipitated as small orange needles, which were collected by filtration and dried in vacuo. Yield: 0.84 g (97%); decomp. at 103°C. − ^{1}H NMR ([D$_8$]THF, 400.1 MHz, 30°C): $\delta = 1.45$ (s, *t*Bu). − ^{13}C NMR ([D$_8$]THF, 100.6 MHz, 30°C): $\delta = 215.3$ ($|J_{P,P}| = 4.7$, $J_{C,P} = 1.3$, $J_{L,Mo} = 86.4$ Hz, CO), 131.8 ($A_2A'X$ system, $|J_{P,P}| = 4.7$, $^1J_{C,P} = 89.9$, $^3J_{C,P} = 4.8$ Hz, ring-C), 41.6 [$|J_{P,P}| = 4.7$, $^2J_{C,P} = 21.7$, $^4J_{C,P} = 0.3$ Hz, $\boldsymbol{C}(CH_3)_3$], 36.12 [$|J_{P,P}| = 4.7$, $^3J_{C,P} = 12.8$, $^1J_{C,H} = 128$ Hz, $C(\boldsymbol{C}H_3)_3$]; all coupling constants were established by simulations. − ^{31}P NMR ([D$_8$]THF, 162 MHz, 30°C): $\delta = 57.6$ (s). − MS (70 eV); *m/z* (%): 482 (29) [M$^+$], 454 (26) [M − CO$^+$], 398 (100) [M$^+$ − 3 CO], 312 (32). − $C_{18}H_{27}O_3P_3Mo$ (480.2): calcd. C 45.02, H 5.65; found C 45.04, H 5.61.

Tricarbonyl(η^6-2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene)-tungsten (12b): To a solution of **9** (200 mg, 0.67 mmol) in THF (3 mL), a solution of tricarbonyl(η^6-toluene)tungsten (**11b**, 285 mg, 0.8 mmol) in THF (2 mL) was added at room temperature. After stirring overnight, the THF was distilled off under reduced pressure (0.5 mbar) and the residue was redissolved in pentane (1 mL). At −78°C, **12b** precipitated as an orange powder, which was collected by filtration and dried in vacuo. Yield: 322 mg (85%); decomp. at 175°C. − ^{1}H NMR ([D$_8$]THF, 200 MHz, 30°C): $\delta = 1.64$ (t, $^4J_{P,H} = 1.5$ Hz, *t*Bu). − ^{13}C NMR ([D$_8$]THF, 50.3 MHz, 30°C): $\delta = 205.1$ ($J_{P,C} = 2.0$, $J_{W,C} = 84.4$ Hz, CO), 127.0 ($^1J_{C,P} = 89.8$, $^3J_{C,P} = 4.0$, $J_{W,C} = 13.5$ Hz, ring-C), 41.9 [$^2J_{P,C} = 21.4$ Hz, $\boldsymbol{C}(CH_3)_3$], 36.0 [$^3J_{P,C} = 12.7$ Hz, $C(\boldsymbol{C}H_3)_3$]. − ^{31}P NMR ([D$_8$]THF, 81.1 MHz, 30°C): $\delta = 38.6$ (s). − MS (70 eV); *m/z* (%): 568 (34) [M$^+$], 540 (100) [M − CO$^+$], 510 (7) [M − 210$^+$], 482 (46) [M − 3 CO$^+$]. − $C_{18}H_{27}O_3P_3W$ (568.1): calcd. C 38.06, H 4.78; found C 38.08, H 4.74.

(η^4-1,5-Cyclooctadiene)(η^6-2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene)ruthenium (14): To a solution of **9** (200 mg, 0.67 mmol) in THF (3 mL), a solution of the ruthenium complex **13** (270 mg, 0.8 mmol) in THF (2 mL) was added at room temperature. After stirring for 4 h, the THF was distilled off at 40°C/0.5 mbar, the residue was redissolved in pentane, and purified by column chromatography (glass column, diameter 2 cm, length 15 cm, silica gel 60, 70−230 mesh, Merck AG). The orange fraction was found to contain complex **14** contaminated by traces of naphthalene. The latter could be removed by sublimation at 60°C/0.5 mbar. The remaining orange powder consisted of pure complex **14**; yield: 275 mg (81%); decomp. at 105°C. − ^{1}H NMR ([D$_8$]THF, 200 MHz, 30°C): $\delta = 3.67$ (br. s, 4 H, COD), 2.03 (br. s, 8 H, COD), 1.52 (s, *t*Bu). − ^{13}C{^{1}H} NMR ([D$_8$]THF, 50.3 MHz, 30°C): $\delta = 132.6$ ($^1J_{P,C} = 87.2$, $^3J_{P,C} = 5.4$ Hz, ring C), 65.1 ($^2J_{P,C} = 1.5$ Hz, COD), 42.7 [$^2J = 22.6$ Hz*, $\boldsymbol{C}(CH_3)_3$], 36.0 [$^3J_{P,C} = 13.2$ Hz*, $C(\boldsymbol{C}H_3)_3$], 33.9 (s, COD); * denotes J by comparison with simulated spectrum of complex **12a**. − ^{31}P NMR ([D$_8$]THF, 81.1 MHz, 30°C): $\delta = 59.0$ (s). − MS (70 eV); *m/z* (%): 510 (25) [M$^+$], 453 (6) [M − *t*Bu$^+$], 402 (100) [M − COD$^+$], 169 (7) [$PC_2t\text{Bu}_2{}^+$], 57 (10) [*t*Bu]. − $C_{23}H_{39}P_3Ru$ (509.6): calcd. C 54.21, H 7.71; found C 54.26, H 7.69.

(η^5-Cyclopentadienyl)(η^6-2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene)manganese (16): To a solution of (η^6-benzene)(η^5-cyclopentadienyl)manganese (**15**, 170 mg, 0.86 mmol) in pentane (3 mL), a solution of **9** (200 mg, 0.67 mmol) in pentane (2 mL) was added at room temperature. From the resulting reaction mixture, complex **16** was separated by column chromatography (eluent: pentane; glass column, diameter 2 cm, length 15 cm, Al_2O_3, Merck AG). The green fraction was found to contain complex **16**, which was obtained as a green oil upon removal of the pentane by distillation. Yield: 40 mg (16%). − ^1H NMR ($[D_8]THF$, 200 MHz, 30°C): $\delta = 4.10$ (s, 5 H, Cp), 1.66 (s, 27 H, *t*Bu). − $^{13}C\{^1H\}$ NMR ($[D_8]THF$, 50.3 MHz, 30°C): $\delta = 134$ (ring C), 70.3 (Cp), 42.3 and 36.0 (*t*Bu). − ^{31}P NMR ($[D_8]THF$, 81.0 MHz, 30°C): $\delta = -4.6$ (s). − MS (70 eV); *m/z* (%): 420 (42) [M^+], 282 (65) [$M - C_2tBu_2^+$], 258 (43) [$M - P_2tBuH^+$], 220 (21) [$M - P_2C_2tBu_2$], 169 (38), 120 (100) [CpMn], 57 (17), 55 (36). − $C_{20}H_{32}P_3Mn$ (420.3): calcd. C 57.15, H 7.64; found C 57.07, H 7.69.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg “Phosphor als Bindeglied verschiedener chemischer Disziplinen”).

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Received July 16, 1998
[I98235]