

Dibenzotropyliene phosphanes (TROPPs): synthesis and coinage metal complexes†

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Dibenzocycloheptatrienyl phosphanes (dibenzotropyliene phosphanes = TROPP^R) **11a–c** may be easily prepared from dibenzocycloheptatrienyl chloride **8** and the secondary phosphanes R₂PH [**9a**: R = Ph; **9b**: R = 4-Me-C₆H₄; **9c**: R = cyclohexyl (Cyc)] in good yields. Alternatively, the di(*tert*-butyl)phosphanyl substituted TROPP^{Bu^t} derivative **4** was obtained along with the phosphane **5** by a mechanistically still unknown rearrangement of a strained phosphorus ylide **I**. The conformations of these new phosphanes were established by X-ray analyses performed for the compounds TROPP^{Bu^t} **4** and TROPP^{Ph} **11a**. The R₂P moiety is bonded to an axial position of the central seven-membered ring, which adopts a boat conformation. Thereby a rigid concave binding site containing a phosphane and an olefin function is formed, which should allow the synthesis of a wide range of transition metal complexes. In order to test how far the particular shape of the TROPP-type ligands enforces metal–olefin interactions, the coinage metal complexes [(TROPP^{Ph})Cu(μ₂-Cl)]₂, **13**, [(TROPP^{Ph})Ag(μ₂-O₂SOClF₃)]₂, **16**, [(TROPP^{Ph})₂Ag][O₃SCF₃], **17** and [(TROPP^{Ph})AuCl], **19** were prepared. These were completely characterized by multinuclear NMR experiments in solution and the solid state, as well as by X-ray analyses. The structural and NMR data show that the interaction between the metal center M and the olefin moiety of the TROPP ligand is weak and decreases in the order Cu > Ag > Au. Indeed, for **19** (M = Au) no interaction could be observed. In the silver complex **17**, coupling between an Ag nucleus and a proton of a bonded olefin was determined for the first time [*J*(^{109/107}Ag, ¹H) = 0.4 Hz]. In solution the complexes derived from TROPP-type ligands seem to have an enhanced (kinetic) stability.

Recently we reported the synthesis of a stable monomeric paramagnetic d⁹-rhodium(0) complex using the novel (dibenzo[*a,d*]cyclohepten-5-yl)diphenyl phosphane (tropylienyldiphenyl phosphane) (**11a**; Scheme 2 *vide infra*) as the ligand.¹ In this article, we report on the synthesis of dibenzotropyliene type phosphanes and their complexation behavior towards the coinage metal ions Cu⁺, Ag⁺ and Au⁺. Previously, Herberhold *et al.* reported the synthesis of the tris(tropylienyldiphenyl)phosphane **12** and the first examples of coordination compounds thereof, such as **2**.³ Independently, and by accident, we found an access to derivatives of this phosphane, namely dibenzotropylienyldi(*tert*-butyl)phosphane **4**, in an attempt to prepare the strained phosphorus ylide **I** from the tricyclic phosphonium salt **3**⁴ (Scheme 1). We will name these phosphanes TROPP^R, where the superscript R indicates the substituent bonded to phosphorus, for example **4** = TROPP^{Bu^t}.

The particular shape of TROPP-type ligands and their electronic characteristics make these phosphanes promising ligands in transition metal chemistry for the following reasons.

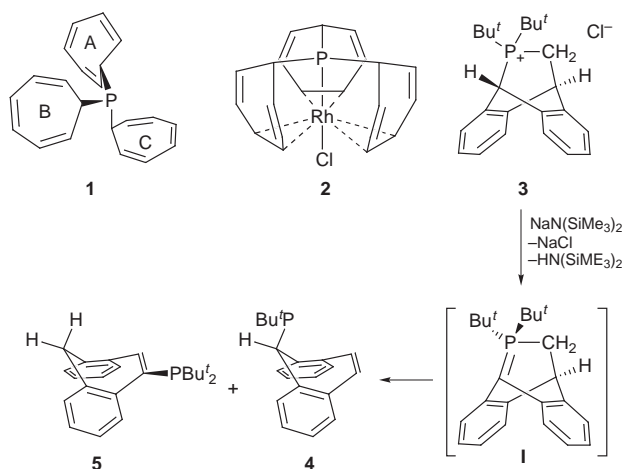
(i) The phosphorus center and the C=C double bond of the cycloheptenyl ring in TROPPs form a stereochemically well-defined concave pocket in which a wide range of transition metals may be hosted.

(ii) The bulky R₂P groups are expected to bind always in the sterically preferred *endo* position of the dibenzotropyliene ring.

(iii) The dibenzotropyliene moiety adopts a rather rigid boat conformation with a high energy barrier for interconversion. This has been thoroughly investigated by means of dynamic NMR spectroscopy for a wide range of substituted cycloheptatrienes.⁵ For TROPPs interconversion barriers higher than 120 kJ mol⁻¹ may be assumed.

(iv) In a first approximation, the phosphorus center serves as a σ-donor ligand while the olefinic moiety acts as a π acceptor. This allows the synthesis of complexes with the metal centers in unusual oxidation states like Rh⁰ or Rh⁻¹.¹

(v) Amino-substituted dibenzotropylienes are very efficient



Scheme 1

† Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

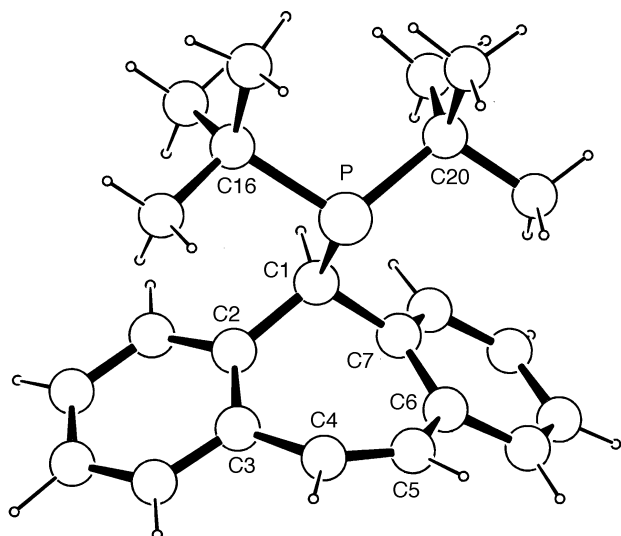


Fig. 1 Molecular structure of **4**. Selected bond lengths and angles are given in Table 1

anti-depressive agents (for example isopavine) and hence the chemistry of benzotropolones is rather well developed.⁶ This will allow the facile synthesis of a wide range of different TROPPs.

(vi) Differently substituted chiral tropolones (which serve as starting materials in Scheme 3, *vide infra*) are natural products⁷ and may be taken as a chiral pool for the synthesis of TROPP enantiomers when required. Moreover, introducing one substituent either in one-half of the hydrocarbon part or at the phosphorus center will break the C_s symmetry of TROPPs like **4** and lead to chiral ligands.

Dibenzotropyliidenyl phosphanes (TROPPs) have some advantages over the tris(cycloheptatrienyl)phosphane **1**, investigated by Herberhold *et al.* The latter is sterically much more flexible. By X-ray analysis and temperature dependent NMR spectroscopy, the axial (ring C in **1**, see Scheme 1) as well as the equatorial binding modes (rings A and B in **1**) of the phosphanyl group have been verified. Furthermore, the presence of nine (!) olefinic units per phosphorus center in **1** shall lead to a diversified and rich but less well-defined coordination chemistry.⁸ In TROPPs, however, the phosphorus center and the single olefinic unit shall serve as preferred binding sites, making the coordination chemistry more predictable. Furthermore, the benzo groups attached to the seven-membered ring lead to funnel-shaped coordination environments around the metal center, facilitating low coordination numbers. In summary, the dibenzotropyliidenyl moiety forming a rigid concave binding site may be regarded as a versatile 'platform', which will allow the investigation of the reactivity of metal centers in electronically very different but well-defined environments.

Does the form of TROPP-type ligands enforce a metal-olefin interaction? To answer this question, we prepared some TROPP complexes of transition metals that form rather stable phosphane complexes but notoriously weak olefin complexes. Therefore, complexes of **11a** and metal ions of the coinage metals Cu, Ag, and Au were prepared.⁹

Results and Discussion

Syntheses

Synthesis of TROPP-type ligands. Preparation of TROPP^{But} **4.** As mentioned above, **4** was first obtained in an attempt to prepare the ylide **I** as shown in Scheme 1. However, in the course of this reaction the phosphanes **4** and **5** were obtained

almost quantitatively in a 40:60 ratio. It is likely that the phosphorus ylide **I** has originally been formed and subsequently underwent a complex rearrangement. The mechanism of this reaction is still unclear and under current investigation. We performed single crystal X-ray analyses of the products **4** and **5** and the results are shown in Fig. 1 and 2, respectively. Selected bond lengths and angles of **4** and **5** are given in Tables 1 and 2, respectively.

The dibenzocycloheptatrienyl moieties in **4** and **5** adopt boat conformations. In **4** the Bu_2P group is bonded to the carbon center at the bow of the boat in an *endo* position with respect to the carbon-carbon double bond at the stern. All P—C bonds are relatively long [average: 1.911(4) Å] due to the steric encumbrance of the phosphorus center. The sum of bond angles at the phosphorus center [$\Sigma(\text{P}) = 313.2^\circ$] is like-

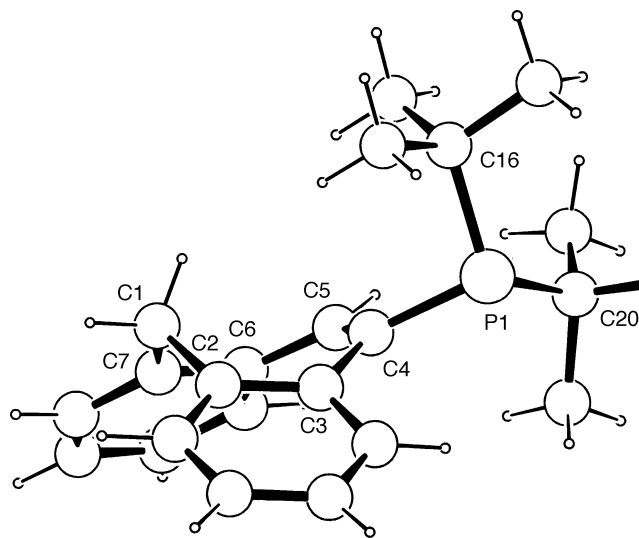


Fig. 2 Molecular structure of **5**. Selected bond lengths and angles are given in Table 2

Table 1 Selected bond lengths (Å) and angles (°) of **4**

P—C20	1.905(4)	C4—C5	1.327(5)
P—C1	1.913(3)	C4—C3	1.465(5)
P—C16	1.914(4)	C5—C6	1.467(5)
C1—C7	1.514(4)	C7—C6	1.401(5)
C1—C2	1.521(4)	C2—C3	1.401(5)
C20—P—C1	102.5(2)	C2—C1—P	112.4(2)
C20—P—C16	109.2(2)	C5—C4—C3	127.7(3)
C1—P—P	101.5(2)	C6—C7—C1	122.2(3)
C7—C1—C2	108.2(3)	C7—C6—C5	123.6(3)
C7—C1—P	115.1(2)	C3—C2—C1	121.9(3)

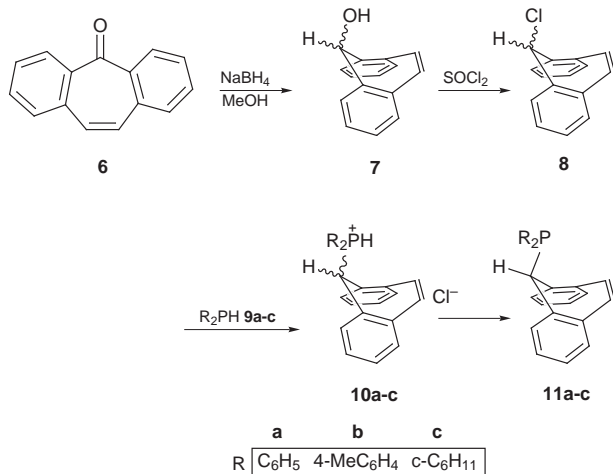
Table 2 Selected bond lengths (Å) and angles (°) of **5**

P1—C4	1.855(2)	C2—C3	1.408(3)
P1—C16	1.890(2)	C3—C4	1.495(2)
P1—C20	1.895(2)	C4—C5	1.348(2)
C1—C2	1.502(3)	C5—C6	1.475(2)
C1—C7	1.505(3)	C6—C7	1.403(2)
C4—P1—C16	100.39(8)	C5—C4—P1	122.86(12)
C4—P1—C20	107.00(8)	C3—C4—P1	114.52(12)
C16—P1—C20	111.79(8)	C4—C5—C6	128.8(2)
C2—C1—C7	109.9(2)	C4—C5—H5	117.4(10)
C3—C2—C1	120.1(2)	C6—C5—H5	113.7(10)
C2—C3—C4	122.0(2)	C7—C6—C5	121.8(2)
C5—C4—C3	122.6(2)	C6—C7—C1	118.9(2)

wise large. As might be expected, there is a considerable bond length alternation within the seven-membered ring. The C4=C5 bond is rather short [1.327(5) Å] while the bonds C4—C3 and C5—C6 to the benzo groups are 1.466(5) Å long. The distances of the C2(7)=C3(6) bonds [1.401(5) Å] belonging to the annulated benzo groups, as well as to the tropyliene ring, are typical for conjugated arene C=C bonds. The remaining two [C1—C2(7)] bonds connecting the arene ring with the bow-carbon center of the seven-membered ring [1.514(4), 1.521(4) Å] correspond to C—C single bonds. These structural features are found in the structures of all compounds discussed in this work. Based on these structural data it may be concluded that the C=C double bond in the tropyliene ring is only weakly conjugated with the benzo groups. In accordance with this assumption, the ^{13}C NMR data of the C2 and C3 carbon centers (132.7 ppm) do not differ significantly from the values found for **1** or tropyliene, C_7C_8 , itself (131.2 ppm). The structural features of the seven-membered carbon cycle in **5** resemble closely the ones observed in **4**, showing the expected bond length alternation, although it is slightly less pronounced compared to **4**. Noteworthy is the length of the C4=C5 double bond [1.348(2) Å] and the sum of bond angles at the phosphorus center (319.2°). Because of the Bu^t_2P group, the ^{13}C NMR resonances of the carbon centers forming the double bond are both shifted to higher frequency (*ca.* 140 ppm) in comparison to **4**.

Preparation of TROPP^{Ph}, 11a, TROPP^{Tol}, 11b and TROPP^{Cyc}, 11c. In a continuation of our work, we searched for a more convenient access to dibenzotropyliidenylphosphanes. Indeed, the synthesis of these ligands is fairly simple and depicted in Scheme 2.

Dibenzotropolone **6** is quantitatively reduced by sodium tetrahydroborate in methanol to give dibenzotropolol **7**, which was used after drying under vacuum without further purification. Subsequently **7** is transformed into the corresponding chloride **8** using thionyl chloride. When a toluene solution of cycloheptenyl chloride **8** is slowly added to a solution of a secondary phosphane R_2PH , **9a–c**, at ambient temperature, a white precipitate of the hydrophosphonium salt, **10a–c**, is formed. At elevated temperature hydrochloride is eliminated and the desired phosphanes **11a–c** are obtained in good yields (70–85%) after recrystallization from acetonitrile. It is advantageous to add the chloride **8** to a solution of phosphane **9** and to perform the reaction in non-polar solvents from which the hydrophosphonium salts precipitate in order to suppress the formation of bis(tropyliidenyl)phosphonium salts, which are undesired side products.² It is noteworthy that solutions of the alcohol **7** and chloride **8** contain *exo/endo*



Scheme 2

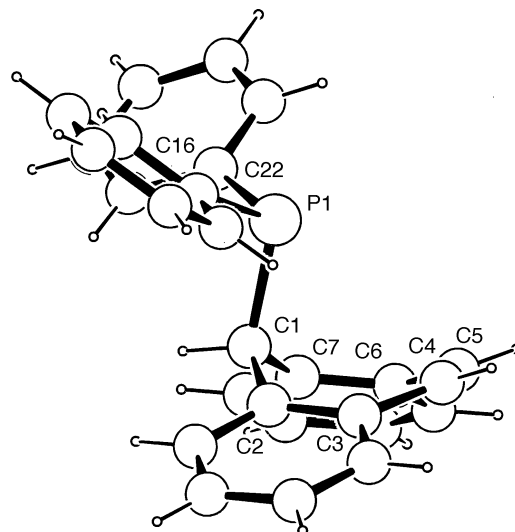


Fig. 3 Molecular structure of **11a**. Selected bond lengths and angles are given in Table 3

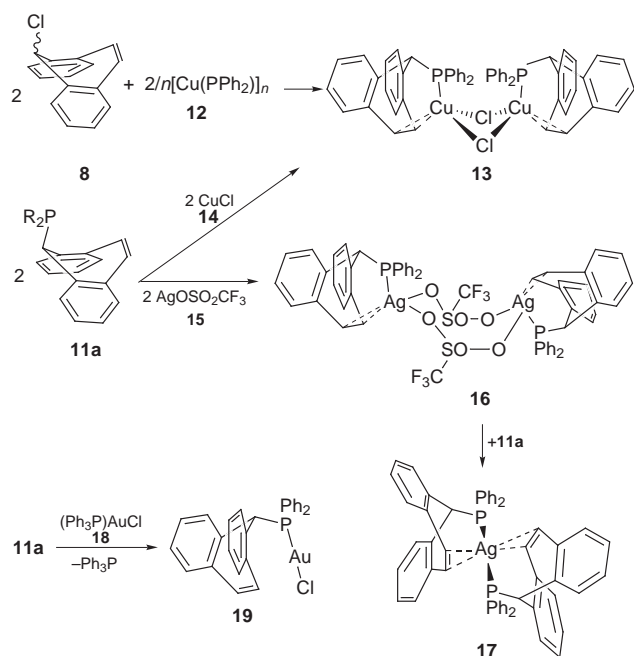
mixtures in which the components interconvert on the NMR timescale, as indicated by the exchange-broadened ^1H NMR resonances at 298 K, while the phosphanes **11a–c** are obtained exclusively in the form of one isomer. In the solid state, this was shown to be the *endo* isomer by X-ray analysis of TROPP^{Ph}, **11a** (Fig. 3), and we assume it maintains the same conformation in solution. Selected bond lengths and angles for **11a** are given in Table 3.

As in TROPP^{Bu^t}, **4**, the phosphanyl group in TROPP^{Ph} is bonded in the axial position of the cycloheptatrienyl ring. The lone pair of electrons at the phosphorus center points towards the C=C double bond. Apart from the smaller sum of bond angles at the phosphorus center (304.3°), which reflects the diminished steric congestion, the molecular shapes of **11a** and **4** are identical within the experimental errors. Hence very similar structures are also inferred for the TROPP^{Tol}, **11b** (Tol = 4-MeC₆H₄), and TROPP^{Cyc}, **11c** (Cyc = cyclohexyl), derivatives. This is further supported by the NMR spectra, which are quite similar for all TROPP^R-type ligands, **4** and **11a–c**. In the ^1H NMR spectra, the resonance signal due to the benzylic hydrogen center bonded adjacent to the phosphorus is observed between 4.50–4.93 ppm [$^2J(^{31}\text{P}^1\text{H}) = 3.4\text{--}6.1\text{ Hz}$]. The olefinic hydrogen centers of the seven-membered ring are observed in the range of 6.76–6.99 ppm and the ^{13}C NMR resonances of the corresponding carbon nuclei are found at 132.7 ± 1 ppm for all TROPP-type ligands prepared so far.

Synthesis of TROPP-coinage metal complexes. The synthesis of the Cu^I , Ag^I and Au^I complexes is summarized in Scheme 3.

Table 3 Selected bond lengths (Å) and angles (°) of **11a**

P1—C22	1.827(3)	C2—C3	1.409(4)
P1—C16	1.837(3)	C3—C4	1.447(4)
P1—C1	1.907(3)	C4—C5	1.328(4)
C1—C7	1.505(4)	C5—C6	1.456(4)
C1—C2	1.507(4)	C6—C7	1.406(4)
C22—P1—C16	103.22(12)	C3—C2—C1	122.4(3)
C22—P1—C1	99.58(12)	C2—C3—C4	123.7(3)
C16—P1—C1	101.50(12)	C5—C4—C3	129.1(3)
C7—C1—C2	115.0(2)	C4—C5—C6	128.9(3)
C7—C1—P1	109.5(2)	C6—C7—C1	122.6(2)
C2—C1—P1	111.4(2)		



Scheme 3

In order to prepare the copper complex **13**, we reacted in THF the chloride **8** with one equivalent of the polymeric copper diphenylphosphide **12**, which can be prepared easily from diphenylphosphane, **9a**, and copper *tert*-butoxide, $[\text{CuOBu}^t]_n$.¹⁰ After recrystallization from acetonitrile, complex **13** is obtained in the form of yellow crystals in about 60% yield. By this reaction we found a third convenient access to TROPP-type ligands. Recently, we reported the introduction of phosphido groups into organic halides by copper reagents, which proved to be a simple method for the synthesis of polyfunctional phosphanes.¹¹ Remarkably, neither the reaction of **8** with lithium diphenylphosphide, LiPPh_2 , nor reactions using the dibenzotropylium salt ($\text{C}_{15}\text{H}_{11}^+$) $[\text{BF}_4^-]$ and **12** or LiPPh_2 gave **11a** in acceptable yields. Instead, complex reaction mixtures were obtained. The ligand is easily liberated from complex **13** by adding a dilute aqueous cyanide solution and extracting the phosphane with an organic solvent. Alternatively, the copper complex **13** can be classically prepared from copper(I) chloride, **14**, and the ligand **11a** in acetonitrile. After recrystallization **13** is obtained in about 70% yield.

Adding a toluene solution of **11a** to a toluene solution of silver triflate (silver trifluoromethanesulfonate), **15**, leads to the mono-TROPP^{Ph} silver complex **16**. Silver triflate is known to form rather stable olefin complexes when compared to silver salts containing other anions.¹² Upon addition of a second equivalent of **11a** to **16** (or by mixing **15** with two equivalents of **11a**) the bis-TROPP^{Ph} silver complex **17** is quantitatively obtained. Both silver complexes form colorless, light-sensitive crystals.

Finally, the gold complex **19** was prepared by a simple ligand-displacement reaction from $(\text{Ph}_3\text{P})\text{AuCl}$, **18**, and **11a**. The TROPP^{Ph} gold complex **19** is obtained in the form of colorless, air-stable crystals in 83% isolated yield.

X-ray crystallography: molecular structures

$[\text{Cu}_2(\mu_2\text{-Cl})_2(\text{TROPP}^{\text{Ph}})_2]$, **13**. The copper compound **13** exists in the solid state in the form of μ_2 -chloride-bridged dinuclear complexes, clathrated with four molecules of acetonitrile, separated by normal van der Waals distances. A SCHAKAL view of the complex is given in Fig. 4, selected bond lengths and angles of **13** are given in Table 4.

The central four-membered Cu_2Cl_2 cycle is folded by 45.7° , allowing a rather short copper-copper distance of $2.832(2)$ Å. Each copper(I) atom lies in the center of a severely distorted

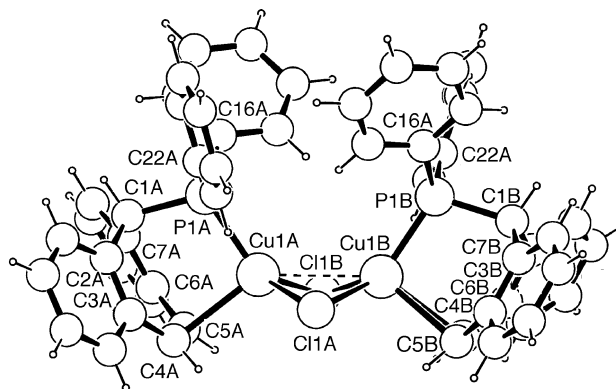


Fig. 4 Molecular structure of **13**. Selected bond lengths and angles are given in Table 4

tetrahedral coordination site formed by the phosphorus and the two chlorine centers as well as by the midpoint of the C=C double bond of the ligand. The copper centers do not bind symmetrically to the olefinic carbon atoms C4 and C5 and thus the Cu—C distances vary from $2.366(4)$ Å to $2.453(4)$ Å [average: $2.413(4)$ Å]. These distances are considerably longer than the Cu—C bond lengths in $[\text{Cu}_2(\mu_2\text{-Cl})_2(\text{COD})_2]$ (2.05 – 2.22 Å) containing a planar Cu_2Cl_2 ring.¹³ The C4=C5 distances in **13** [average: $1.353(5)$ Å] are only slightly longer than in the free ligand **11a** [$1.328(4)$ Å] but are much shorter than the complexed C=C bond in $[\text{Cu}_2(\mu_2\text{-Cl})_2(\text{COD})_2]$ (1.41 Å).¹⁴ The Cu—P distances [average: $2.216(2)$ Å] and the Cu—Cl distances [average: $2.348(2)$ Å] lie in the range expected for Cu^I compounds.¹³ The rather long P—C bond between the phosphorus center and the carbon atom of the seven-membered ring in **11a** [$1.907(3)$ Å] becomes a little shorter upon complexation of the phosphorus center in **13** [$1.874(4)$ Å]. The sum of C—P—C bond angles in **13** is slightly increased by 7.4° [$\Sigma(\text{P}) = 311.8^\circ$]. The only significant structural indication for a copper-olefin interaction is thus the deviation from planarity of the copper center from its P,Cl,Cl coordination sphere. Assuming the absence of a copper-olefin interaction, trigonal planar coordination by the phosphorus and two chlorine centers is expected, which as a result would give 360° as the sum of the two P—Cu—Cl and the Cl—Cu—Cl angles. In **13**, these sums of bond angles amount to 344.9° and 343.7° at Cu1A and Cu1B, respectively, which can

Table 4 Selected bond lengths (Å) and angles ($^\circ$) of **13**

Cu1A—P1A	2.213(2)	C2A—C3A	1.407(5)
Cu1A—Cl1A	2.3397(13)	C3A—C4A	1.462(5)
Cu1A—Cl1B	2.347(2)	C4A—C5A	1.351(5)
Cu1A—C5A	2.408(4)	C5A—C6A	1.468(5)
Cu1A—C4A	2.453(4)	C6A—C7A	1.408(5)
Cu1A—Cu1B	2.832(2)	P1B—C1B	1.879(4)
Cu1B—P1B	2.2180(14)	C1B—C2B	1.511(5)
Cu1B—Cl1B	2.3426(13)	C1B—C7B	1.512(5)
Cu1B—Cl1A	2.362(2)	C2B—C3B	1.403(5)
Cu1B—C5B	2.366(4)	C3B—C4B	1.468(6)
Cu1B—C4B	2.425(4)	C4B—C5B	1.355(5)
P1A—C1A	1.869(4)	C5B—C6B	1.468(5)
C1A—C2A	1.510(5)	C6B—C7B	1.411(5)
C1A—C7A	1.513(5)		
P1A—Cu1A—Cl1A	121.31(5)	P1B—Cu1B—Cl1A	125.59(5)
P1A—Cu1A—Cl1B	125.12(6)	Cl1B—Cu1B—Cl1A	97.95(5)
Cl1A—Cu1A—Cl1B	98.46(6)	P1B—Cu1B—C5B	95.50(10)
P1A—Cu1A—C5A	94.47(10)	Cl1B—Cu1B—C5B	122.73(10)
Cl1B—Cu1A—C5A	89.37(10)	P1B—Cu1B—C4B	92.98(11)
P1A—Cu1A—C4A	93.53(10)	Cl1B—Cu1B—C4B	97.41(10)
Cl1A—Cu1A—C4A	101.40(10)	Cu1A—Cl1A—Cu1B	74.10(5)
P1B—Cu1B—Cl1B	120.17(5)	Cu1B—Cl1B—Cu1A	74.32(5)

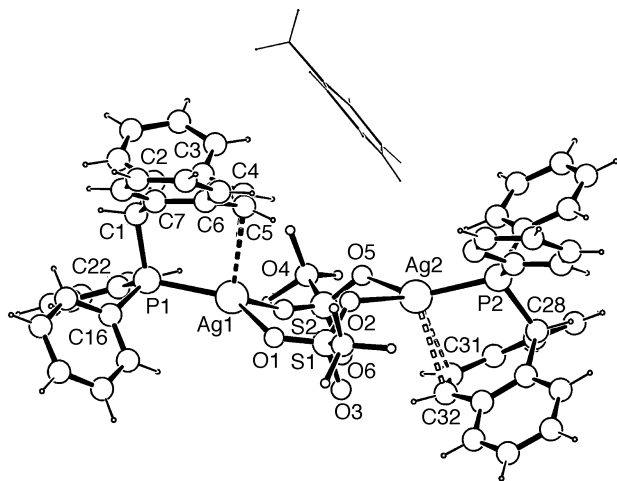


Fig. 5 Molecular structure of **16**. Selected bond lengths and angles are given in Table 5

be taken as a useful indicator to estimate the strength of the metal–olefin interaction (for a non-distorted tetrahedron the sum of these three bond angles amounts to 322.5°). The crystal used for the X-ray analysis contained a dinuclear copper complex in which both phosphorus centers are located on the same side of the mean Cu(μ₂-Cl)₂Cu plane. The possible existence of additional isomeric structures in the bulk material was investigated by means of ³¹P CP-MAS NMR (*vide infra*).

[Ag₂(μ₂-O₂SOCF₃)₂(TROPP^{Ph})₂], **16**. Crystals of the monophosphane silver compound **16** were obtained from toluene solutions and contain one molecule of clathrated toluene, which is shown by thin lines in Fig. 5. In the solid state, **16** crystallizes as a neutral dinuclear complex. A SCHAKAL view of **16** is given in Fig. 5, while relevant bond lengths and angles are compiled in Table 5.

Owing to severe disordering of the CF₃ groups of the CF₃SO₃ moieties, the structure could not be satisfactorily re-

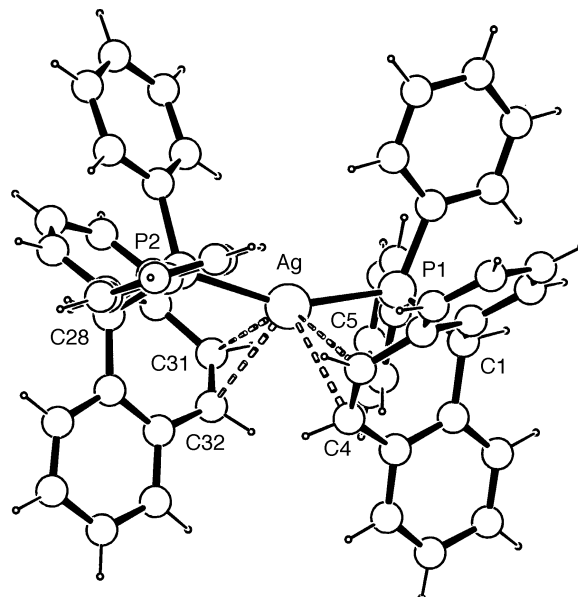


Fig. 6 Molecular structure of **17**. Selected bond lengths and angles are given in Table 6

fined and the obtained data have limited value. Nevertheless, some trends can be discussed. The triflate units each use two oxygen centers to bridge two silver centers such that an eight-membered ring is formed, which adopts a semi *anti*-crown conformation as found, for instance, in S₈²⁺. The Ag–P bonds [2.364(3) Å; 2.358(3) Å] are longer by about 0.15 Å compared to the Cu–P distances in **13** but are shorter than other reported Ag–P distances (2.42 Å).^{14a} The Ag–C bonds (2.711–2.858 Å) in **13** are very long when compared to the averaged distances of many silver olefin complexes (2.4–2.5 Å).^{14a,15} The very weak silver–olefin interaction is well-expressed by the sum of the two O–Ag–P and O–Ag–O bond angles [Ag1: 355.5°; Ag2: 352.3°], which indicate only very little displacement of the silver(i) centers from the trigonal planar coordination caused by a silver–olefin interaction. The slightly larger sums of C–P–C bond angles in **16** [Σ(P) = 315.7°] are in accord with the larger complex formation constants of silver-phosphane complexes when compared to copper complexes.¹²

[Ag(TROPP^{Ph})₂]₂O₃SCF₃, **17**. Crystals of the TROPP^{Ph} silver complex **17** were obtained after recrystallization from toluene. A SCHAKAL view of the cation of the complex is shown in Fig. 6, selected bond lengths and angles are listed in Table 6.

In this complex two ligand molecules are coordinated to the silver ion and there is no contact with the triflate counter anion. The anion and a co-crystallized toluene molecule are strongly disordered, which again diminishes the quality of the data. Linearly coordinated silver-bisphosphane complexes have been observed very often in the solid state.¹⁶ In **17**, the particular steric requirements of the TROPP^{Ph} ligand, **11a**, enforce a considerable deviation from linear coordination by about 26° [P–Ag–P 154.2(1)°]. In comparison to the monophosphane complex **16**, the Ag–P bond distances (average:

Table 5 Selected bond lengths (Å) and angles (°) of **16**

Ag1–O4	2.264(11)	C5–C4	1.34(2)
Ag1–O1	2.358(8)	S1–O1	1.405(10)
Ag1–P1	2.364(3)	S1–O3	1.412(9)
P1–C22	1.795(13)	O2–Ag2	2.333(10)
P1–C16	1.813(12)	Ag2–O5	2.327(11)
P1–C1	1.880(10)	Ag2–P2	2.358(3)
C1–C7	1.496(15)	P2–C28	1.860(11)
C1–C2	1.51(2)	C32–C31	1.32(2)
C7–C6	1.41(2)	S2–O4	1.361(11)
C6–C5	1.45(2)	S2–O5	1.418(10)
C2–C3	1.38(2)	S2–O6	1.568(11)
C3–C4	1.47(2)		
O4–Ag1–O1	100.8(4)	C4–C5–C6	128.0(12)
O4–Ag1–P1	127.8(3)	C5–C4–C3	128.6(13)
O1–Ag1–P1	126.9(3)	O2–S1–O1	113.7(6)
C22–P1–C16	106.0(6)	O2–S1–O3	116.5(7)
C22–P1–C1	103.9(5)	O1–S1–O3	114.0(7)
C16–P1–C1	105.8(5)	S1–O1–Ag1	119.5(5)
C22–P1–Ag1	116.0(4)	S1–O2–Ag2	129.5(6)
C16–P1–Ag1	114.5(4)	O5–Ag2–O2	89.6(4)
C1–P1–Ag1	109.6(4)	O5–Ag2–P2	133.2(3)
C7–C1–C2	115.1(9)	O2–Ag2–P2	129.5(3)
C7–C1–P1	112.5(7)	C28–P2–Ag2	109.4(4)
C2–C1–P1	110.7(7)	O4–S2–O5	115.9(8)
C6–C7–C1	121.5(12)	O4–S2–O6	114.8(8)
C7–C6–C5	125.0(12)	O5–S2–O6	113.7(7)
C3–C2–C1	123.1(11)	S2–O4–Ag1	160.1(9)
C2–C3–C4	124.7(12)	S2–O5–Ag2	125.4(6)

Table 6 Selected bond lengths (Å) and angles (°) of **17**

Ag–P2	2.392(2)	C4–C5	1.333(14)
Ag–P1	2.402(3)	P2–C28	1.89
P1–C1	1.868(9)	C31–C32	1.31
C1–C2	1.533(13)		
P2–Ag–P1	154.2(1)	C28–P2–Ag	112.0(1)
C1–P1–Ag	112.3(3)		

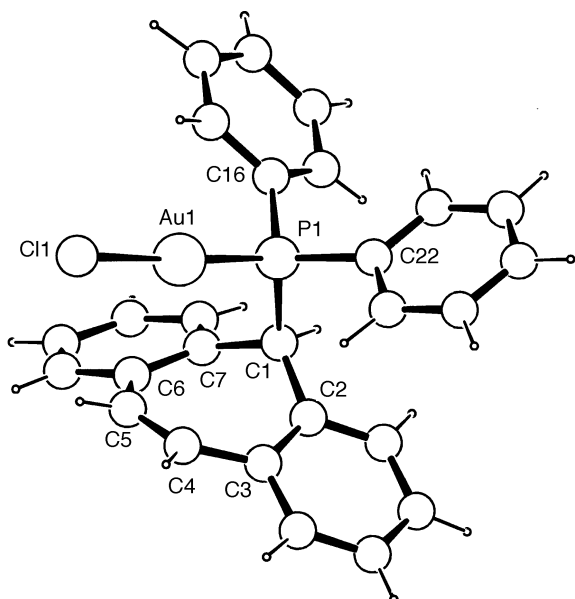


Fig. 7 Molecular structure of **19**. Selected bond lengths and angles are given in Table 7

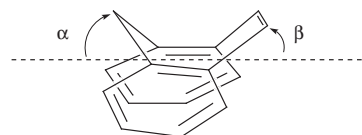
2.397 Å) are, as expected, slightly longer. Again, the Ag—C bonds are very long [2.77(1)–2.88(1) Å] and no significant changes of the C=C distances [1.31(1) Å and 1.33(1) Å] compared to the free ligand **11a** are observed within the experimental errors.

[AuCl(TROPP^{Ph})], 19. In Fig. 7 the result of an X-ray analysis of the gold TROPP^{Ph} complex **19** is shown; selected bond lengths and angles are compiled in Table 7.

There are no reports on authentic gold–olefin complexes and as can be seen from the almost linear P—Au—Cl coordination [177.59(4)°] in **19**, any significant gold–olefin interaction is not reflected by an expected deviation from linear coordination. The Au—C distances in **19** [3.095(3) and 3.286(3) Å] are only slightly shorter than the sum of the van der Waals radii (3.35 Å). It might be possible that a gold–olefin interaction can be enforced by abstracting chloride from **19** with a Lewis acid or by replacing chloride with a weakly coordinating anion; however, attempts to isolate such a species have failed so far. The Au—P distance [2.234(2) Å] is expectedly shorter than the Ag—P distances in **16** and **17**.^{14a} There are no further special structural features that distinguish complex **19** from other phosphane gold(I) chloride complexes.¹⁶ No gold–gold separations below 3.5 Å are observed in crystals of **19**, which is a phenomenon often estab-

Table 7 Selected bond lengths (Å) and angles (°) of **19**

Au1—P1	2.234(2)	C1—C7	1.517(6)
Au1—Cl1	2.300(2)	C2—C3	1.419(6)
P1—C16	1.811(4)	C3—C4	1.450(7)
P1—C22	1.816(5)	C4—C5	1.329(7)
P1—C1	1.873(5)	C5—C6	1.460(7)
C1—C2	1.512(6)	C6—C7	1.412(7)
P1—Au1—Cl1	177.59(4)	P1—C1—H1	105(3)
C16—P1—C22	108.4(2)	C3—C2—C1	123.6(4)
C16—P1—C1	102.1(2)	C2—C3—C4	123.6(4)
C22—P1—C1	105.0(2)	C5—C4—C3	129.4(5)
C16—P1—Au1	112.6(2)	C5—C4—H4	114(3)
C22—P1—Au1	113.1(2)	C3—C4—H4	117(3)
C1—P1—Au1	114.7(2)	C4—C5—C6	129.9(5)
C2—C1—C7	116.3(4)	C4—C5—H5	121(3)
C2—C1—P1	114.1(3)	C6—C5—H5	109(3)
C7—C1—P1	109.8(3)	C7—C6—C5	123.8(4)
C2—C1—H1	106(3)	C6—C7—C1	123.0(4)
C7—C1—H1	105(3)		



Scheme 4

lished and referred to as ‘aurophilicity’ in many gold phosphane complexes and clusters.¹⁷

A further structural criterion to study the metal–olefin interaction in complexes **13**, **16**, **17** and **19** is change of the boat conformation of the seven-membered ring system of the TROPP ligand, which may be circumscribed by the angles α and β (Scheme 4). These parameters for the uncomplexed ligands **4** and **11a** and the coinage metal complexes **13**, **16**, **17** and **19** are listed for comparison in Table 8.

It is clearly seen that the complexation of the metal centers Cu⁺, Ag⁺ and Au⁺ has very little influence on the boat form when compared to that of the free ligand **11a**. In the copper complex **13**, the shape of the ligand is slightly more compressed and in the gold complex it is slightly widened compared to free **11a**. This observation corresponds with the expectation that the copper center will bind weakly to the olefinic moiety while the gold center shows no measurable binding interaction. Interestingly, the sterically more encumbered phosphane TROPP^{Bu}, **4**, has a considerably more folded structure than **11a**. This may be explained by repulsive interactions of the spatially more extended *tert*-butyl groups with the annulated benzo rings, which are thereby bent away from the phosphorus substituents. The form of ring C in (C₇H₇)₃P, **1** (Scheme 1), in which the P center occupies the axial position as in **4** and **11a** has comparable angles α and β .

NMR spectroscopy

Solid state NMR spectroscopy of [Cu₂(μ₂-Cl)₂(TROPP^{Ph})₂], 13. The experimental ³¹P solid state NMR spectrum, recorded under the conditions of cross-polarization and rapid rotation about the ‘magic angle’, is depicted in Fig. 8(a).

Two well-resolved ‘quartet’ patterns at δ_{iso} = 22 and –25 in a ratio of ca. 8:3 are observed in the isotropic region of the spectrum. Based on the crystal structure analysis of **13**, showing the presence of two crystallographically inequivalent phosphorus sites, one would also expect to find two different isotropic chemical shifts in the ³¹P NMR spectrum. However, the intensity distribution actually observed makes such an interpretation unlikely. Indeed, reconsidering the molecular structure of **13** one finds that the two sites are almost, but not quite, related by a C₂ symmetry. Therefore, we have to interpret the spectrum as originating from either two different stereoisomers, for example, as *E* and *Z* forms of [Cu₂(μ₂-Cl)₂(TROPP^{Ph})₂] or, alternatively, a single isomeric form occurring in two different crystallographic modifications. One of these could be as for **13**, that is, containing clathrated acetonitrile molecules, while the other is solvent-free. Measuring a ³¹P solid state NMR spectrum immediately after recrystallization results in a spectrum different from the one above, showing a single, but somewhat broadened, ‘quartet’ pattern at δ_{iso} = 20. Subjecting this material to ageing under vacuum reproduces qualitatively the original two-component

Table 8 Comparison of folding angles α and β (°) in TROPP complexes and ligands

	13	16	17	19	11a	4	1
M	Cu	Ag	Ag	Au	—	—	—
α	48.3	46.6	48.9	44.9	47.8	53.2	46.2
β	24.6	21.7	22.6	22.7	24.4	26.2	23.5

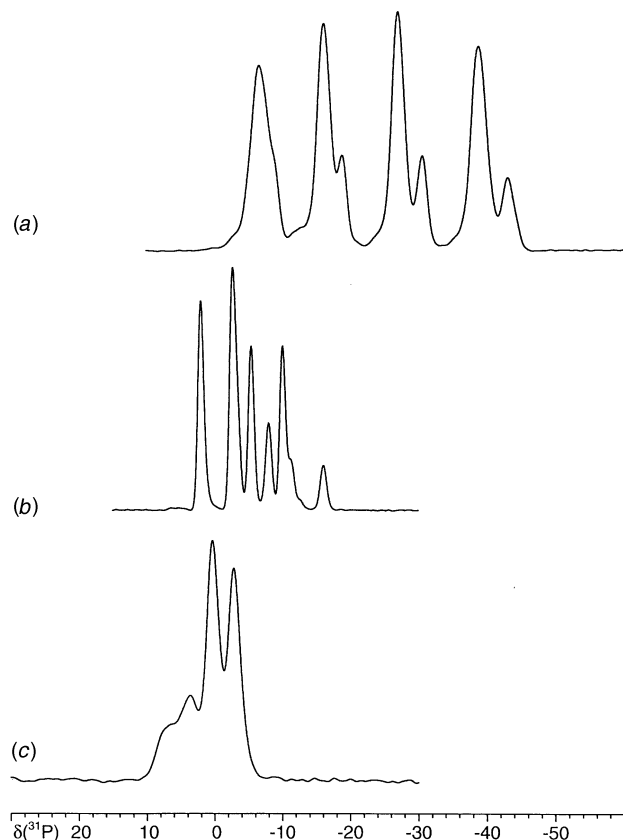


Fig. 8 CP-MAS- ^{31}P NMR spectra of (a) copper complex **13**, (b) silver complex **16** and (c) silver complex **17**

spectrum, in agreement with an assignment to different crystallographic modifications rather than different isomers.

Each of the above mentioned 'quartets' is of a typical asymmetric form, both with respect to the separations of the multiplet lines as well as the individual line shapes. Such patterns, arising from the interaction of a spin 1/2 nucleus with the spins 3/2 of the ^{65}Cu and ^{63}Cu nuclei, have been analyzed before¹⁸ and a convenient first-order analysis has been derived.¹⁹ The latter approximation allows us to estimate the scalar coupling constants $^1J_{^{65}\text{Cu},^{31}\text{P}}$ and $^1J_{^{63}\text{Cu},^{31}\text{P}}$, which are evaluated to be 1865 and 1740 Hz for the major component and 1990 and 1860 Hz for the minor component. The magnitude of these coupling constants are within the range previously observed^{20,21} for 'cubane'-type tetramers of composition $\text{CuCl}(\text{PR}_3)_3$, showing severely distorted tetrahedral coordination sites with a CuCl_3P environment. Significantly smaller values for the parameter $^1J_{^{63}\text{Cu},^{31}\text{P}}$, that is, *ca.* 1270 and 940 Hz, have been found for tetrahedral CuCl_2P_2 and CuClP_3 environments.²⁰ This indicates that the loosely coordinated double bond in **13** exerts an electronic influence on $^1J_{^{63}\text{Cu},^{31}\text{P}}$, which is similar to that of a bridging chloride rather than that of a phosphorus ligand.

Solid state NMR spectroscopy of $[\text{Ag}_2(\mu_2\text{-O}_2\text{SOCF}_3)_2(\text{TROPP}^{\text{Ph}})_2]$, **16.** The isotropic region of the solid state NMR spectrum recorded for **16** shows four discernible doublets at $\delta = 0, -5, -8$ and -13 with relative intensities of 12:5:9:3 [see Fig. 8(b)]. Each of the doublets arises from overlapping unresolved doublets due to the coupling to the ^{109}Ag and ^{107}Ag spins with a magnitude of *ca.* 750 Hz, which is close to the average of 770 Hz of $^1J_{^{31}\text{P},^{109}\text{Ag}}$ and $^1J_{^{31}\text{P},^{107}\text{Ag}}$ observed at low temperature in CDCl_3 solution. As a sample of **16**, freshly crystallized from toluene and immediately measured, showed only one doublet at $\delta = -9$ with an averaged Ag,P coupling constant of 778 Hz, one should assign the former spectrum to one isomeric form of the complex confined to a crystallographically variable environment.

Solid state NMR spectroscopy of $[\text{Ag}(\text{TROPP}^{\text{Ph}})_2]\text{O}_3\text{SCF}_3$, **17.** The isotropic region of the solid state NMR spectrum of **17** consists of two sets of signals at $\delta = 5$ and -2 [see Fig. 8(c)]. The former, being broad and of a not well-defined shape, originates possibly from the overlap of two ABM, $M = ^{109}\text{Ag}$ and ^{107}Ag , spin systems and is also present in a freshly crystallized sample. The latter consists of a doublet with a spacing of 503 Hz, which is in close agreement with the average phosphorus silver couplings, that is, 522 Hz, observed for **17** in CDCl_3 solution and possibly represents again a different crystallographic modification of the same complex **17**.

Solution NMR spectroscopy of TROPP complexes. Selected ^1H , ^{13}C and ^{31}P NMR data of **11a**, **13**, **16**, **17** and **19** are listed in Table 9 for comparison.

Some significant changes are observed in the NMR data when the free TROPP^{Ph} ligand, **11a**, is complexed by a coinage metal. As frequently observed, the ^{31}P NMR resonance is shifted towards higher frequencies with increasing main quantum number of the metal in the order $\text{Cu} < \text{Ag} < \text{Au}$.²² The $^2J_{^{31}\text{P},^1\text{H}}$ coupling between the phosphorus nucleus and the benzylic proton, which is small in the free phosphane **11a**, increases by about 6–10 Hz upon complexation. This is an expected trend when the coordination number at phosphorus is augmented. However, the strong decrease of the $^1J_{^{31}\text{P},^{13}\text{C}}$ coupling constant from 20.9 Hz in **11a** to 12.7 Hz in the copper complex **13** to less than 0.5 Hz in the silver and gold complexes **16**, **17** and **19** where no coupling could be resolved, is an unexpected phenomenon and has not been observed in transition metal complexes of $(\text{C}_7\text{H}_7)_3\text{P}$, **1**.^{2,10} The presence of a copper, silver or gold center in close proximity (< 2.5 Å) to the $\text{C}=\text{C}$ double bond of the heptatrienyl moiety has merely an influence on the chemical shift of the ^1H or ^{13}C NMR resonances of this unit, especially when solvent effects are taken into account.²³ At best, a minor low frequency shift by about 2–3 ppm can be observed in the ^{13}C NMR spectra of the complexes. However, the rigid conformation of the TROPP ligand allowed, for the first time, the estimation of a ^{109}Ag , ^1H coupling constant within an olefin-silver(i) complex. In a ^{109}Ag , ^1H heteronuclear multiple quantum coherence spectrum of complex **17** (Fig. 9) a cross-

Table 9 Selected ^1H , ^{13}C and ^{31}P NMR data of **11a**, **13**, **16**, **17** and **19**. δ is *vs.* TMS (^1H , ^{13}C) or 85% H_3PO_4 (^{31}P). $J(^{31}\text{P}, ^1\text{H})$ and $J(^{31}\text{P}, ^{13}\text{C})$ coupling constants in Hz are given in parentheses

	Solvent	^1H NMR δ CH(2J)	^1H NMR δ HC=CH	^{13}C NMR δ CH(1J)	^{13}C NMR δ HC=CH(4J)	^{31}P NMR
11a	C_6D_6	4.78 (6.1)	6.76	57.4 (20.9)	132.7 (5.1)	-14.9
13	CD_3CN	5.40 (12.6)	> 7.10	55.4 (12.7)	128.9 (2.2)	-14.6
16	C_6D_6	4.75 (15.6)	6.53	56.8 (<0.5)	127.8 (<0.5)	-3.0
17	C_6D_6	5.39 (12.3)	6.77	55.8 (<0.5)	129.6 (<0.5)	1.5
19	NC_5D_5	5.92 (16.8)	> 7.00	56.0 (<0.5)	129.2 (<0.5)	31.2

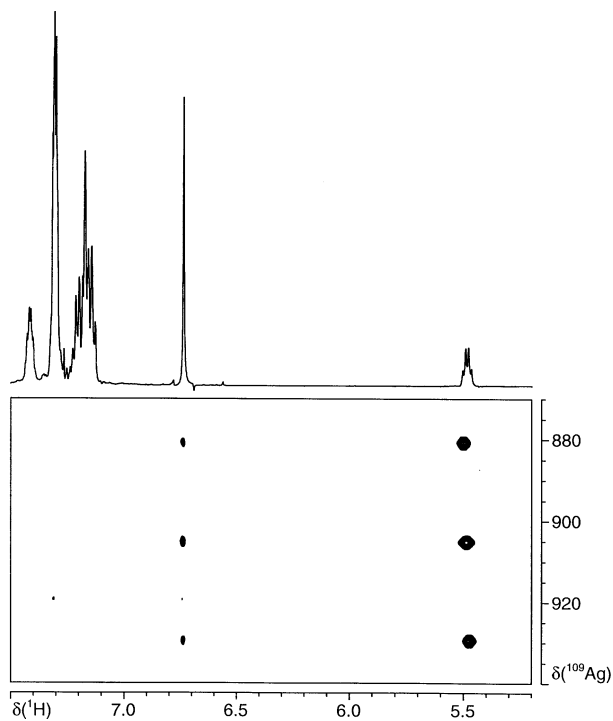
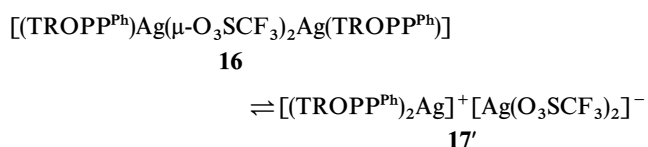


Fig. 9 $^{109}\text{Ag}, ^1\text{H}$ heteronuclear multiple quantum coherence spectrum of complex **17**

peak due to an unresolved geminal coupling between the ^{109}Ag spin with the ^1H olefinic spins could be observed.

As there is an additional vicinal coupling to the phosphorus spins, the magnitude of the parameter $^2J_{^{109}\text{Ag}, ^1\text{H}}$ could be evaluated from data obtained in a $^{31}\text{P}, ^1\text{H}$ heteronuclear correlation experiment and $^2J_{^{109}\text{Ag}, ^1\text{H}}$ amounts to *ca.* 0.4 Hz. The vicinal, $^3J_{^{109}\text{Ag}, ^1\text{H}}$, coupling between the ^{109}Ag nucleus and the benzylic proton adjacent to the phosphorus center in the same compound is larger, and of opposite sign, and amounts to 7.3 Hz.

We have furthermore investigated the stability of the silver(I) TROPP^{Ph} complexes **16** and **17** in solution by ^{31}P NMR spectroscopy. The spectrum of a CDCl_3 solution of complex **16** at 298 K shows one broad doublet centered at -3.0 ppm, which is resolved into two doublets at a temperature of 243 K [Fig. 10(a)]. The doublets are caused by coupling of the ^{31}P spin with the ^{107}Ag (spin 1/2, 51.8% abundance) and ^{109}Ag (spin 1/2, 48.2% abundance) spins. Large coupling constants of 721 Hz ($^1J_{^{107}\text{Ag}, ^{31}\text{P}}$) and 830 Hz ($^1J_{^{109}\text{Ag}, ^{31}\text{P}}$) in **16** have been observed before for complexes in which silver(I) binds to one tertiary phosphane ligand.²⁴ At the higher temperature of 323 K, only one broad resonance signal is observed, indicating non-rigid behavior. Cross-peaks observed between all ^{31}P resonances in a ^{31}P exchange spectrum clearly demonstrate that the exchange process is intermolecular in that one ^{31}P spin is associated with both the ^{107}Ag and the ^{109}Ag spins. This can be explained by a dissociation-complexation equilibrium in which the ligand with its ^{31}P spin is statistically distributed over both silver spins. The displacement of the average chemical shift towards higher frequency indicates an equilibrium of the following form involving the species **17'** rather than free phosphane:



This explanation is also in agreement with the following experiments. The bis(TROPP^{Ph}) silver complex **17** (containing

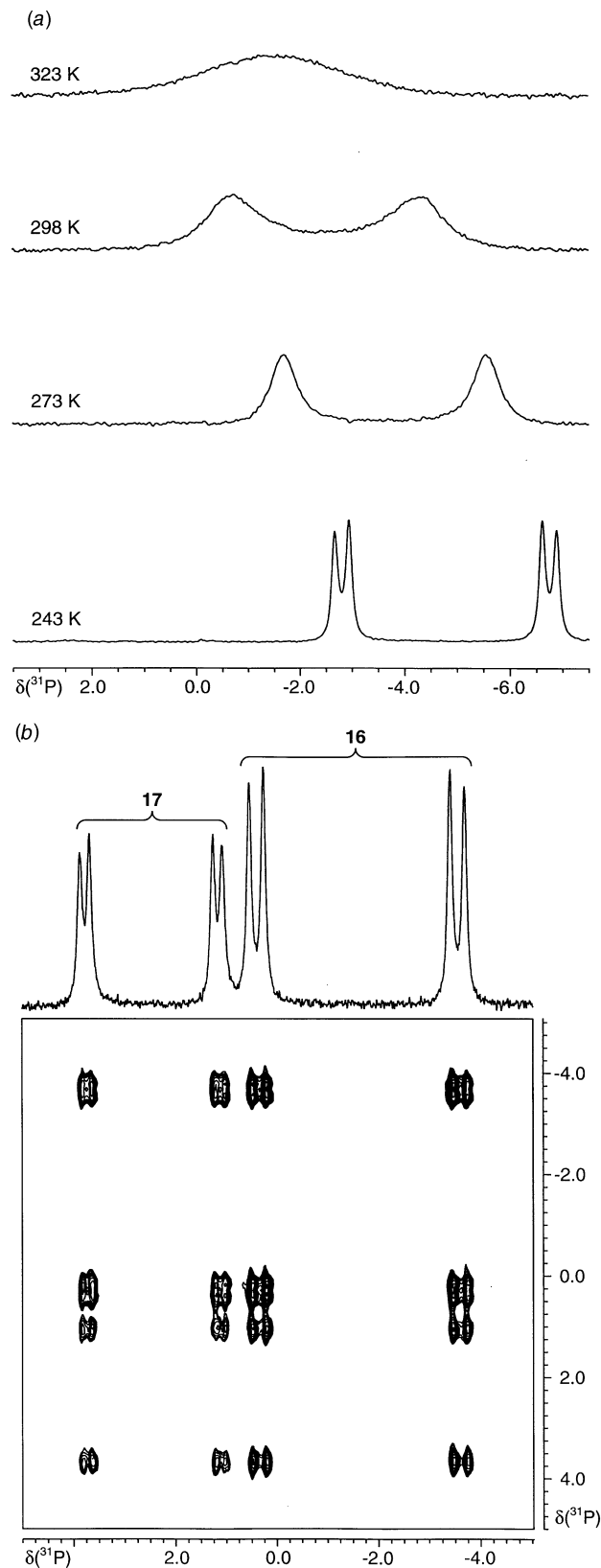
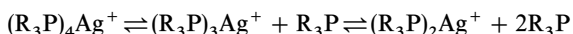


Fig. 10 (a) ^{31}P NMR spectrum of a CDCl_3 solution of complex **16** at different temperatures; (b) ^{31}P exchange spectrum of a CDCl_3 solution of a mixture of complexes **16** and **17** at 298 K

the same cation as **17'**) shows two doublets centered at 1.5 ppm in solution. The $^{109}\text{Ag}, ^{31}\text{P}$ and $^{107}\text{Ag}, ^{31}\text{P}$ coupling constants amount to 491 Hz and 567 Hz, respectively, and lie in the typical range observed for bisphosphane complexes of silver.²⁵ In solutions of pure **17**, ligand-exchange processes were not observed by NMR experiments. Adding silver tri-

flate, **15**, to a solution of **17** leads, within the timescale of the experiment, to rapid formation of the monophosphane complex **16** by ligand exchange. In mixtures, both complexes **16** and **17** can be observed separately by ^{31}P NMR spectroscopy, indicating slow ligand exchange on the NMR timescale. That exchange indeed takes place, could be again demonstrated in a ^{31}P exchange spectrum where cross-peaks between all resonances were observed [Fig. 10(b)]. The slow ligand exchange between TROPP^{Ph} silver complexes is all the more remarkable as other silver tertiary phosphane complexes show rapid equilibria of the form:²⁵



Monophosphane silver complexes of the type R_3PAg^+ were not detected in these latter studies. Only for silver bisphosphane complexes containing a chelating ligand like *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ could well-resolved ^{31}P NMR spectra showing all couplings be recorded at room temperature.²⁶

If an excess of triphenylphosphane Ph_3P is added to a CDCl_3 solution of **16**, a broadened resonance signal at +8.6 ppm and a broadened doublet at -1.1 ppm with a $^{107/109}\text{Ag}$ coupling of ca. 330 Hz is observed. This experiment indicates that, although exchange does occur, even a large excess of Ph_3P does not liberate the TROPP^{Ph} ligand **11a** from the silver center to a significant extent and the most prominent species is likely to be a $[(\text{TROPP}^{\text{Ph}})\text{Ag}(\text{PPh}_3)]^+[\text{O}_3\text{SCF}_3]^-$ complex. Usually, the phosphane with the smaller cone angle Θ [$\Theta(\text{PPh}_3) = 145^\circ$] replaces the phosphane with the larger one. We have estimated²⁷ the cone angles Θ of **4** and **11a-c** by applying the trigonometric procedure developed by Imyanitov²⁸ using parameters from X-ray data obtained for **4** and **11a** and the reported increments for phenyl (Ph), *tert*-butyl (Bu^t), cyclohexyl (Cyc) and *p*-tolyl (*p*Tol) substituents. Assuming, that TROPP^R, **4**, and **11a-c** act as monodentate ligands, cone angles of 210° (**4**), 185° (**11a, b**) and 201° (**11c**) are estimated. However, regarding TROPP ligands as chelates leads to estimations²⁸ of much smaller cone angles of 151° (**4**), 127° (**11a, b**) and 143° (**11c**). These values may be compared to those of bulky monodentate phosphanes like Bu^t_3P ($\Theta = 182^\circ$) and Cy_3P ($\Theta = 170^\circ$) or of bidentate ligands like $\text{Ph}_2\text{P}-\text{CH}_2-\text{CH}_2-\text{PPh}_2$ ($\Theta = 125^\circ$) and $\text{Cy}_2\text{P}-\text{CH}_2-\text{CH}_2-\text{PCy}_2$ ($\Theta = 142^\circ$).²⁹ One may therefore conclude that TROPP ligands act as chelate ligands (smaller Θ) and hence are not replaced by bulkier monodentate phosphanes.

In summary, the NMR spectroscopic results obtained for the silver complexes **16** and **17**, together with the observation that the gold complex **19** is quantitatively formed by a ligand-displacement reaction from Ph_3PAuCl , may be taken as an indication of at least an increased kinetic stability of TROPP^R metal complexes.

Conclusion

Dibenzo(tropylidenyl)phosphanes (TROPP^R) are a new class of phosphanes that may serve as ligands for the preparation of *cis*-phosphane olefin metal complexes. They can be easily prepared in good yields from dibenzotropylidenylchloride, **8**, and a secondary phosphane HPR_2 . NMR spectra of all TROPP-type ligands prepared so far reveal that only one stereoisomer is formed, which is the *endo* isomer with the R_2P group axially bonded to the cycloheptatrienyl moiety. The new phosphanes are rigid and show no interconversion on the NMR timescale. From studies of the properties of TROPP^R coinage metal complexes, it may be concluded that the complexes possess at least an enhanced kinetic stability when compared to other phosphane complexes. The interaction of the metal centers Cu, Ag and Au is rather weak, as is indicated by the NMR and structural data, and follows the order $\text{Cu} > \text{Ag} > \text{Au}$. This is different from the stability order of cationic ethylene

complexes $[\text{Cu}(\text{H}_2\text{C}=\text{CH}_2)]^+$, $[\text{Ag}(\text{H}_2\text{C}=\text{CH}_2)]^+$ and $[\text{Au}(\text{H}_2\text{C}=\text{CH}_2)]^+$ for which recent gas phase experiments and theoretical investigations established a stability ordering of $\text{Au} > \text{Cu} > \text{Ag}$.³⁰ In TROPP-type ligands the phosphane donor function is arranged almost orthogonally to the olefin moiety of the tropyliene ring. Using the R_2P group as an anchor point, it might be possible to prepare and isolate models of cationic $[\text{M}(\text{R}_2\text{C}=\text{CR}_2)]^+$ complexes in the condensed phase, in which the olefin-metal interaction is electronically relatively unperturbed. These, as well as studies of the olefin interaction with metals of the first transition metal series (which are relatively rare), are under way. Owing to the well-developed organic chemistry of dibenzotropylidenes, TROPP ligands offer the possibility to study the properties of metal centers in electronically widely tunable but stereochemically well-defined environments.

Experimental

General methods

All operations were carried out under an atmosphere of dry and oxygen-free nitrogen by modified Schlenk techniques. Solvents were dried by standard methods,³¹ distilled and stored under nitrogen. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F , $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at room temperature in C_6D_6 , CDCl_3 , CD_3CN , $\text{C}_5\text{D}_5\text{N}$ or $\text{C}_4\text{D}_8\text{O}$ on Bruker AC200, DPX250, DPX300, DRX400, AMX500 and Varian Unity-300 instruments. ^{109}Ag data were obtained in an indirect way by two-dimensional $^{109}\text{Ag}, ^1\text{H}$ HMQC (heteronuclear multiple quantum coherence) spectroscopy. Chemical shifts, in ppm are given relative to TMS for ^1H and ^{13}C , CFCl_3 for ^{19}F , 85% aqueous H_3PO_4 for ^{31}P and aqueous Ag^+ for ^{109}Ag , extrapolated to infinite dilution. Solid state ^{31}P NMR spectra were recorded by employing spinning at the 'magic' angle, with spinning frequencies between 2 and 14 kHz, and cross-polarization using contact times between 0.5 and 4 ms on a Bruker AMX400 equipped with a solid state accessory. Chemical shifts are given relative to $(\text{NH}_4)_2\text{H}_2\text{PO}_4$. Melting points are uncorrected, determined by sealing single crystals of the compounds, under inert atmosphere, inside melting point capillaries and by measuring in a melting point apparatus according to Mr. Tottoli. Mass spectra were recorded on a Finnigan MAT 8200 operating in either the EI (70 eV) or CI mode. Raman spectra were recorded on a Bruker FT-IR IFS 66V equipped with a Raman accessory R106 (Neodym-YAG Lasers, 1064 nm). IR spectra were recorded as thin films (for liquids) between carefully dried NaCl plates, or as pellets (powder + KBr) on a Perkin-Elmer 783 spectrometer.

Precursor compounds like the dibenzo[*a,d*]cyclohepten-5-yl derivatives **7** and **8**,³² diphenylphosphane **9a**,³³ ditolylphosphane **9b**,^{34,35} and dicyclohexylphosphane **9c**³⁶ (the alcohol and the chloride) were synthesized according to the literature. Dibenzosuberenone **6** was purchased in reagent grade from Aldrich.

Crystallographic analysis of **4**, **5**, **11a**, **13**, **16**, **17** and **19**

The data sets for the single-crystal X-ray studies were collected on Nonius CAD4 and fully automated Siemens-Stoe AED2 four-circle diffractometers. All calculations were performed on a Digital Corporation VAX system, using the SHELXS 86 and SHELXL 93 programs.^{37,38} The specific data for the crystals and the refinements are collected in Tables 10 and 11. The structures were solved by direct methods and refined by full-matrix least-squares on F_2 .

The graphical representations of the molecular structures were drawn using the SCHAKAL program.³⁹ Further crystallographic data (excluding structure factors) for the structures

Table 10 Crystal data and structure refinement for **4**, **5** and **11a**

	4	5	11a
Empirical formula	C ₂₃ H ₂₉ P	C ₂₃ H ₂₉ P	C ₂₇ H ₂₁ P
Formula weight	336.43	336.43	376.44
Temperature/K	293(2)	203(2)	293(2)
Wavelength/Å	0.71069	0.71070	0.71069
Space group	<i>Fdd2</i>	<i>P2(1)/c</i>	<i>P1</i>
Crystal system	Orthorhombic, face-centered	Monoclinic	Triclinic
Unit cell dim./Å, °	<i>a</i> = 23.072(5), α = 90 <i>b</i> = 37.029(7), β = 90 <i>c</i> = 9.179(2), γ = 90	<i>a</i> = 8.788(4), α = 90 <i>b</i> = 14.205(7), β = 92.70(3) <i>c</i> = 16.021(8), γ = 90	<i>a</i> = 10.4162(12), α = 93.617(8) <i>b</i> = 10.7631(11), β = 90.830(8) <i>c</i> = 18.841(2), γ = 101.975(8)
Volume/Å ³	7842(3)	1998(2)	2061.4(4)
<i>Z</i>	16	4	4
Absorption coeff./mm ⁻¹	0.141	0.139	0.141
Reflections collected	2126	5829	7682
Independent reflections	1216 [<i>R</i> (int) = 0.0000]	5829 [<i>R</i> (int) = 0.0000]	7246 [<i>R</i> (int) = 0.0263]
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0394, <i>wR</i> 2 = 0.0888	<i>R</i> 1 = 0.0490, <i>wR</i> 2 = 0.0975	<i>R</i> 1 = 0.0482, <i>wR</i> 2 = 0.1084
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0726, <i>wR</i> 2 = 0.1044	<i>R</i> 1 = 0.0974, <i>wR</i> 2 = 0.1146	<i>R</i> 1 = 0.1246, <i>wR</i> 2 = 0.1446

reported in this paper have been deposited with the Fachinformationszentrum Karlsruhe as supplementary publication No. CSD-406944 (**4**), CSD-406941 (**5**), CSD-406945 (**11a**), CSD-406946 (**13**), CSD-406947 (**16**), CSD-406943 (**17**) and CSD-406942 (**19**).

CCDC reference number 440/054.

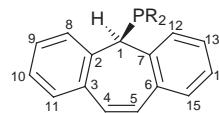
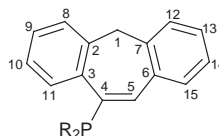
Synthesis of the ligands

Phosphanes 4 and 5 by reaction of dibenzo-7-phosphonium-bicyclo[2.2.2]octadiene chloride 3 with NaN(SiMe₃)₂. One gram (2.7 mmol) of dibenzo-7-phosphonium-bicyclo[2.2.2]octadiene chloride **3** was dried overnight *in vacuo* at 60 °C. The powdered substance was then suspended in 20 ml of toluene at −78 °C and 0.5 g (2.7 mmol) of sodium bistrimethylsilylamide, dissolved in 20 ml of toluene, was added dropwise. While warming up to ambient temperature a dark brown solid and a bright yellow solution were formed. After 1 h stirring at ambient temperature the brown solid residue was filtered off and the yellow solution (containing only two products according to a ³¹P NMR spectrum) was reduced under vacuum to dryness. The residue was fractionally recrystallized from acetonitrile to yield **4** and **5**. Hereby single crystals suitable for X-ray diffraction of both compounds could be obtained. Performing the reaction under different conditions (other temperatures or in THF as solvent) did not alter the results.

(Dibenzo[*a,d*]cyclohepten-5-yl)di(*tert*-butyl)phosphane (TROPP^{Bu}), **4** (Scheme 5): yield 290 mg (32%); mp 188–190 °C. ¹H NMR (C₆D₆, 200.13 MHz): δ 0.86 (d, ³*J*_{PH} = 9.7 Hz, 18H, CH₃), 4.67 (d, ²*J*_{PH} = 3.4 Hz, 1H, C₁H), 6.94 (m, 2H, C_{9,13}H), 6.99 (s, 2H, C_{4,5}H), 7.03–7.10 (m, 4H, C_{10,14}H and C_{11,15}H), 7.16 (m, 2H, C_{8,12}H). ¹³C NMR (C₆D₆, 75.43

MHz): δ 31.2 (d, ²*J*_{PC} = 14.1 Hz, CH₃), 33.3 (d, ¹*J*_{PC} = 33.2 Hz, CMe₃), 51.6 (d, ¹*J*_{PC} = 37.8 Hz, C₁), 126.2 (s, C_{9,13}), 128.8 (s, C_{11,15}), 129.4 (d, ⁵*J*_{PC} = 1.7 Hz, C_{10,14}), 129.5 (d, ³*J*_{PC} = 2.3 Hz, C_{8,12}), 132.7 (d, ⁴*J*_{PC} = 6.0 Hz, C_{4,5}), 136.4 (d, ³*J*_{PC} = 2.8 Hz, C_{3,6}), 140.1 (d, ²*J*_{PC} = 7.8 Hz, C_{2,7}). ³¹P NMR (C₆D₆, 81.01 MHz): δ 26.8. MS(EI): *m/z* 336 (**4**, 5%), 191 (dibenzotropyliumion, 100%), 57 (*tert*-butyliumion, 14%).

(Dibenzo[*a,d*]cyclohepten-10-yl)di(*tert*-butyl)phosphane, **5** (Scheme 6): yield 435 mg (48%); mp 145 °C. ¹H NMR (C₆D₆, 200.13 MHz): δ 1.20 (br, 9H, CH₃), 1.38 (br, 9H, CH₃), 3.58 (s, 2H, C₁H), 7.00–7.15 (m, 7H, C_{8–10}H and C_{12–15}H), 7.61 (d, ³*J*_{PH} = 3.1 Hz, 1H, C₅H), 8.40 (m, 1H, C₁₁H). ¹³C NMR (C₆D₆, 50.32 MHz): δ 29.9 (br, CH₃), 31.1 (br, CH₃), 33.0 (br, CMe₃), 41.4 (s, C₁), 125.6 (d, ⁴*J*_{PC} = 1.4 Hz, C₁₀), 125.8 (s, C₉), 126.9 (d, ⁴*J*_{PC} = 1.4 Hz, C₈), 126.9 (d, ³*J*_{PC} = 1.7 Hz, C₁₁), 127.8 (d, ²*J*_{PC} = 2.0 Hz, C₅), 128.0 (s, C₁₄), 128.6 (s, C₁₅), 129.8 (s, C₁₃), 130.4 (s, C₁₂), 134.9 (s, C₇), 139.1 (d, ³*J*_{PC} = 5.3 Hz,

**Scheme 5** Numbering scheme for NMR spectra of **4**, **11a–c**, **13**, **16**, **17**, **19****Scheme 6** Numbering scheme for NMR spectra of **5****Table 11** Crystal data and structure refinement for **13**, **16**, **17** and **19**

	13	16	17	19
Empirical formula	C ₆₂ H ₅₄ Cl ₂ Cu ₂ N ₄ P ₂	C _{66.50} H ₅₄ Ag ₂ F ₆ O ₆ P ₂ S ₂	C ₅₅ H ₄₂ AgF ₃ O ₃ P ₂ S	C ₂₇ H ₂₁ AuClP
Formula weight	1115.01	1404.90	1009.81	608.82
Temperature/K	200(2)	293(2)	293(2)	203(2)
Wavelength/Å	0.71073	0.71069	0.71069	0.71070
Space group	<i>P1</i>	<i>P2(1)/c</i>	<i>P2(1)/c</i>	<i>P2(1)/n</i>
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Unit cell dim./Å, °	<i>a</i> = 12.848(5), α = 110.92(4) <i>b</i> = 13.826(7), β = 96.00(4) <i>c</i> = 17.827(9), δ = 106.34(3)	<i>a</i> = 20.708(4), α = 90 <i>b</i> = 19.978(4), β = 105.79(3) <i>c</i> = 15.561(3), δ = 90	<i>a</i> = 20.455(4), α = 90 <i>b</i> = 17.143(3), β = 108.00(3) <i>c</i> = 16.653(3), δ = 90	<i>a</i> = 10.378(7), α = 90 <i>b</i> = 18.350(12), β = 92.36(5) <i>c</i> = 11.603(8), δ = 90
Volume/Å ³	2763(2)	6195(2)	5554(2)	2208(3)
<i>Z</i>	2	4	8	4
Absorption coeff./mm ⁻¹	0.967	0.820	0.502	6.869
Reflections collected	15703	5939	5338	3883
Independent reflections	8086 [<i>R</i> (int) = 0.0293]	5704 [<i>R</i> (int) = 0.0264]	5149 [<i>R</i> (int) = 0.0680]	3883 [<i>R</i> (int) = 0.0000]
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0435, <i>wR</i> 2 = 0.1125	<i>R</i> 1 = 0.0499, <i>wR</i> 2 = 0.1263	<i>R</i> 1 = 0.0701, <i>wR</i> 2 = 0.1837	<i>R</i> 1 = 0.0253, <i>wR</i> 2 = 0.0586
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0531, <i>wR</i> 2 = 0.1247	<i>R</i> 1 = 0.1082, <i>wR</i> 2 = 0.1641	<i>R</i> 1 = 0.1089, <i>wR</i> 2 = 0.2259	<i>R</i> 1 = 0.0323, <i>wR</i> 2 = 0.0615

C₂), 139.5 (d, ³J_{PC} = 3.1 Hz, C₆), 139.7 (d, ¹J_{PC} = 12.8 Hz, C₄), 140.4 (d, ²J_{PC} = 3.8 Hz, C₃). ³¹P NMR (C₆D₆, 81.01 MHz): δ 37.5. MS(EI): *m/z* 336 (5, 60%), 280 (5 – Bu⁺ + H, 30%), 224 (5 – 2Bu⁺ + 2H, 100%), 191 (dibenzotropyliumion, 85%), 178 (anthraceniumion, 52%), 57 (*tert*-butyliumion, 22%), 43 (isopropylumion, 30%).

Preparation of tropylidene phosphanes 11a–c

(TROPP^{Ph}), 11a. To a solution of 5.0 g (26.9 mmol) of diphenylphosphane **9a** in 20 ml of toluene, a solution of 6.1 g (26.9 mmol) of dibenzo[*a,d*]cyclohepten-5-yl chloride **8** in 20 ml of toluene was slowly added at ambient temperature. A white solid precipitated. After 1 h stirring at ambient temperature the mixture was refluxed for 15 h under evolution of gaseous HCl. The obtained reaction mixture was hot-filtered and the solvent was removed *in vacuo*. The white solid residue was then recrystallized from acetonitrile whereby colorless crystals suitable for X-ray diffraction could be obtained. Yield 7.1 g (70%); mp 140–142 °C. ¹H NMR (C₆D₆, 299.95 MHz): δ 4.78 (d, ²J_{PH} = 6.1 Hz, 1H, C₁H), 6.76 (m, 2H, C_{4,5}H), 6.82–6.88 (m, 8H, *p*-H_{ph}, *m*-H_{ph} and C_{10,14}H), 6.88–6.94 (m, 4H, C_{9,13}H and C_{11,15}H), 6.98–7.60 (m, 2H, C_{8,12}H), 7.24–7.33 (m, 4H, *o*-H_{ph}). ¹³C NMR (C₆D₆, 75.43 MHz): δ 57.4 (d, ¹J_{PC} = 20.9 Hz, C₁), 126.6 (d, ⁴J_{PC} = 1.1 Hz, C_{9,13}), 128.1 (s, *p*-C_{ph}), 128.5 (s, *m*-C_{ph}), 128.6 (s, C_{10,14}), 130.0 (d, ³J_{PC} = 2.2 Hz, C_{8,12}), 130.6 (d, ⁴J_{PC} = 3.3 Hz, C_{11,15}), 132.7 (d, ⁴J_{PC} = 5.1 Hz, C_{4,5}), 134.2 (d, ²J_{PC} = 20.9 Hz, *o*-C_{ph}), 135.9 (d, ³J_{PC} = 4.9 Hz, C_{3,6}), 138.2 (d, ¹J_{PC} = 23.6 Hz, PC_{ph}), 138.5 (d, ²J_{PC} = 10.1 Hz, C_{2,7}). ³¹P NMR (CDCl₃, 81.01 MHz): δ –14.9. MS(EI): *m/z* 376 (11a, 25%), 191 (dibenzotropyliumion, 100%).

(TROPP^{Tol}), 11b. In a similar manner, the reaction was carried out with 3.7 g (17.7 mmol) of di-*p*-tolylphosphane **9b** and 4 g (17.7 mmol) of dibenzo[*a,d*]cyclohepten-5-yl chloride **8**. Colorless crystalline needles were isolated after crystallization from a mixture of acetonitrile and toluene. Yield 5.2 g (73%); mp 220–223 °C. ¹H NMR (C₆D₆, 200.13 MHz): δ 2.00 (s, CH₃), 4.93 (d, ²J_{PH} = 5.4 Hz, 1H, C₁H), 6.73–7.00 (m, 10H, C_{4,5}H, *m*-H_{tol}, C_{9,13}H, C_{10,14}H and C_{11,15}H), 7.02–7.15 (m, 2H, C_{8,12}H), 7.35 (dd, ³J_{PH} = 6.9 Hz, ³J_{HH} = 6.9 Hz, *o*-H_{tol}). ¹³C NMR (C₆D₆, 50.32 MHz): δ 21.1 (s, CH₃), 57.5 (d, ¹J_{PC} = 20.9 Hz, C₁), 126.5 (d, ⁴J_{PC} = 2.1 Hz, C_{9,13}), 128.3 (d, ³J_{PC} = 1.3 Hz, *m*-C_{tol}), 128.9 (s, C_{10,14}), 130.0 (d, ³J_{PC} = 2.2 Hz, C_{8,12}), 130.7 (d, ⁴J_{PC} = 3.2 Hz, C_{11,15}), 132.7 (d, ⁴J_{PC} = 4.8 Hz, C_{4,5}), 134.3 (d, ²J_{PC} = 20.9 Hz, *o*-C_{tol}), 134.8 (d, ¹J_{PC} = 20.7 Hz, PC_{tol}), 135.9 (d, ³J_{PC} = 5.2 Hz, C_{3,6}), 138.3 (s, CH₃-C_{tol}), 138.5 (d, ²J_{PC} = 9.6 Hz, C_{2,7}). ³¹P NMR (C₆D₆, 81.01 MHz): δ –16.4. MS(EI): *m/z* 404 (11b, 30%), 191 (dibenzotropyliumion, 100%).

(TROPP^{Cy}), 11c. In a similar manner, the reaction was carried out with 1.5 g (7.5 mmol) dicyclohexylphosphane **9c** and 1.7 g (7.5 mmol) of dibenzo[*a,d*]cyclohepten-5-yl chloride **8**. Colorless needles crystallized from acetonitrile. Yield 2.4 g (82.5%); mp 184–185 °C. ¹H NMR (C₆D₆, 200.13 MHz): δ 0.87–1.18 (brm, 8H, H_{cy}), 1.20–1.40 (brm, 6H, H_{cy}), 1.53–1.60 (brm, 6 H, H_{cy}), 1.78–1.84 (brm, 2H, CP-H_{cy}), 4.50 (d, ²J_{PH} = 4.9 Hz, 1H, C₁H), 6.95 (s, 2H, C_{4,5}H), 7.00–7.20 (m, 8H, C_{8–15}H). ¹³C NMR (C₆D₆, 75.43 MHz): δ 26.9 (s, *p*-C_{cy}), 27.9 (d, ³J_{PC} = 10.4 Hz, *m*-C_{cy}), 28.1 (d, ³J_{PC} = 7.7 Hz, *m*-C_{cy}), 30.0 (d, ²J_{PC} = 8.8 Hz, *o*-C_{cy}), 31.2 (d, ²J_{PC} = 17.5 Hz, *o*-C_{cy}), 35.3 (d, ¹J_{PC} = 23.6 Hz, PC_{cy}), 52.2 (d, ¹J_{PC} = 26.9 Hz, C₁H), 126.4 (d, ⁴J_{PC} = 0.8 Hz, C_{9,13}), 128.6 (s, C_{10,14}), 129.6 (d, ³J_{PC} = 1.8 Hz, C_{8,12}), 129.9 (d, ⁴J_{PC} = 0.7 Hz, C_{11,15}), 132.6 (d, ⁴J_{PC} = 3.3 Hz, C_{4,5}), 136.1 (d, ³J_{PC} = 2.6 Hz, C_{3,6}), 139.8 (d, ²J_{PC} = 5.5 Hz, C_{2,7}). ³¹P NMR (C₆D₆, 81.01 MHz): δ –3.2. MS(EI): *m/z* 388 (11c, 70%), 306 (11c – cyclohexyl + H, 95%), 224 (11c – 2 cyclohexyl + 2 H, 20%), 191

(dibenzotropyliumion, 100%), 178 (anthraceniumion, 48%).

Preparation of 11a (TROPP^{Ph}) using copper phosphide 12

Copper(i) diphenylphosphide **12**¹¹ (1.34 g, 5.4 mmol) was suspended in 20 ml of THF and 1.24 g (5.4 mmol) of dibenzo[*a,d*]cyclohepten-5-yl chloride **8**, dissolved in 10 ml of THF, was slowly added. After a few minutes of stirring the suspension became a clear yellow solution. The solvent was removed under vacuum and the yellow solid residue was suspended in 20 ml of CH₂Cl₂. A saturated aqueous solution of KCN was then added slowly and the mixture was stirred until two clear colourless phases formed. The organic phase was separated, dried with anhydrous Na₂SO₄ and concentrated under vacuum. The colorless solid residue was recrystallized from a minimum amount of warm acetonitrile to yield 1.16 g (57%) of **11a**, which is soluble in toluene and dichloromethane.

Synthesis of TROPP metal complexes

[(TROPP^{Ph})₂Cu^ICl₂]·4CH₃CN, 13. 300 mg (0.79 mmol) of TROPP^{Ph}, **11a** was dissolved in 5 ml of acetonitrile and added at ambient temperature to a suspension of 78 mg (0.79 mmol) of copper(i) chloride (CuCl) in *ca.* 30 ml of acetonitrile. The mixture was warmed up to about 40–50 °C for a short time, yielding a clear yellow solution. At 4 °C yellow crystals suitable for an X-ray diffraction study were formed and filtered off. Yield 300 mg (68%); mp > 224 °C decomposes. Anal. calcd for C₆₂H₅₄Cl₂Cu₂N₄P₂ (1115.09): C, 66.78; H, 4.88; N, 5.02; P, 5.56; Cl, 6.36%. Found: C, 66.79; H, 4.68; N, 4.82; P, 5.78; Cl, 6.65%. ¹H NMR (CD₃CN, 200.13 MHz): δ 5.40 (d, ²J_{PH} = 12.6 Hz, 1H, C₁H), 7.10–7.35 (m, 16H, C_{4,5}H, *m*-, *p*-H_{ph} and C_{8–15}H), 7.58 (m, 4H, *o*-H_{ph}). ¹³C NMR (CD₃CN, 75.43 MHz): δ 55.4 (d, ¹J_{PC} = 12.7 Hz, C₁), 128.9 (d, ⁴J_{PC} = 2.2 Hz, C_{4,5}), 129.1 (d, ⁴J_{PC} = 4.9 Hz, C_{9,13}), 130.0 (d, ³J_{PC} = 9.4 Hz, C_{8,12}), 130.8 (d, ⁵J_{PC} = 1.5 Hz, C_{10,14}), 131.4 (d, ⁴J_{PC} = 2.3 Hz, C_{11,15}), 131.9 (d, ⁴J_{PC} = 1.7 Hz, *p*-C_{ph}), 132.4 (d, ³J_{PC} = 4.9 Hz, *m*-C_{ph}), 133.2 (d, ¹J_{PC} = 26.4 Hz, PC_{ph}), 135.8 (d, ³J_{PC} = 15.4 Hz, C_{3,6}), 136.3 (d, ²J_{PC} = 6.1 Hz, *o*-C_{ph}), 136.9 (d, ²J_{PC} = 3.9 Hz, C_{2,7}). ³¹P NMR (CD₃CN, 81.01 MHz): δ –14.6.

Preparation of (TROPP^{Ph})₂Ag^I₂(O₃SCF₃)₂, 16. To a solution of 100 mg (0.39 mmol) of silver(i) triflate [Ag(O₃SCF₃)₂] **15** in 10 ml of toluene a solution of 146.3 mg (0.39 mmol) of TROPP^{Ph}, **11a**, in 10 ml of toluene was added dropwise at ambient temperature. After a few minutes of stirring, the solvent was reduced under vacuum to one-third of its volume and the solution was kept in the dark at room temperature. The colorless crystals formed were filtered off yielding 152.7 mg (62%) of **16**, mp > 160 °C decomposes. Before elemental analysis, the crystals were powdered and dried under vacuum for 36 h. Anal. calcd for C₅₆H₄₂Ag₂F₆O₆P₂S₂ (1266.76): C, 53.10; H, 3.34%. Found: C, 52.59; H, 3.38%. ¹H NMR (C₆D₆, 200.13 MHz): δ 4.75 (d, ²J_{PH} = 15.6 Hz, 1H, C₁H), 6.53 (s, 2H, C_{4,5}H), 6.72 (t, ³J_{HH} = 7.3 Hz, 2H, C_{9,13}H), 6.80 (t, ³J_{HH} = 7.6 Hz, 2H, C_{10,14}H), 6.88 (br, 4H, *m*-H_{ph}), 6.95–7.02 (m, 2H, C_{11,15}H), 7.06–7.20 (m, 6H, *p*-H_{ph} and *o*-H_{ph}), 7.42 (s, 2H, C_{8,12}H). ¹³C NMR (C₆D₆, 75.43 MHz): δ 56.8 (s, C₁), 127.8 (s, C_{4,5}), 128.5 (s, C_{9,13}), 128.7 (s, C_{10,14}), 129.3 (s, C_{8,12}), 130.8 (s, C_{11,15}), 130.9 (s, *p*-C_{ph}), 131.5 (s, *m*-C_{ph}), 131.7 (d, ²J_{PC} = 4.0 Hz, *o*-C_{ph}), 134.0 (d, ²J_{PC} = 2.5 Hz, C_{3,6}), 134.4 (d, ¹J_{PC} = 16.1 Hz, PC_{ph}), 134.8 (d, ²J_{PC} = 6.4 Hz, C_{2,7}). ¹⁹F NMR (CDCl₃, 75.43 MHz): δ –77.7. ³¹P NMR (CDCl₃, 81.012 MHz): δ –3.0 (dd, ¹J_{107AgP} = 720.7 Hz, ¹J_{109AgP} = 829.2 Hz).

[(TROPP^{Ph})₂Ag^I]₂O₃SCF₃, 17. Complex **17** was prepared like **16** but using **15** and **11a** in a 1:2 stoichiometry [250 mg (0.97 mmol) **15** and 730.5 mg (1.95 mmol) **11a**; each component dissolved in 10 ml of toluene]. Colorless single crystals suitable for X-ray diffraction were obtained by slow diffusion

of hexane into a solution of complex **17** in toluene. This compound has to be stored as well in the dark. Yield of $C_{55}H_{42}AgF_3O_3P_2S$ (1009.81): 931 mg (95%); mp > 150 °C decomposes. 1H NMR ($CDCl_3$, 200.13 MHz): δ 5.48 (A parts of 2 AA'MM'X spin systems, $^4J_{PH} + ^2J_{PH} = 12$ Hz, $^3J_{AgH} = 7.0$ Hz, 1H, C_{1H}), 6.74 (s, $^2J_{AgH} < 1$ Hz, 2H, $C_{4,5H}$), 7.15 (m, $C_{8,12H}$), 7.18 (m, $C_{9,13,10,14H}$), 7.21 (m, $p-C_{phH}$), 7.31 (m, $o-C_{phH}$ and $m-C_{phH}$), 7.42 (m, $C_{11,15H}$). ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ 55.3 (A parts of 2 AMM'X systems, $^1J_{PC} + ^3J_{PC} = 15$ Hz, $J_{AgC} \approx 2$ Hz, C_1), 121.2 (q, $^1J_{FC} = 321$ Hz, CF_3), 128.0 (br s, $p-C_{ph}$), 128.4 (m, A parts of 2 AMM'X systems, $^1J_{PC} + ^3J_{PC} = 31.4$ Hz, $J_{AgC} \approx 5$ Hz, PC_{ph}), 129.0 (A parts of 2 AMM'X systems, $^3J_{PC} + ^5J_{PC} = 10.1$ Hz, $m-C_{ph}??$), 129.4 (br m, $C_{4,5}$), 130.3 (s, $C_{10,14}$), 130.4 (s, $C_{9,13}$), 131.3 (s, $C_{11,15}$), 131.7 (br m, A parts of 2 AMM'X systems, $^3J_{PC} + ^5J_{PC} = 5$ Hz, $C_{8,12}$), 133.4 (br m, A parts of 2 AMM'X systems, $^3J_{PC} + ^5J_{PC} = 5$ Hz, $C_{3,6}$), 133.8 (m, A parts of 2 AMM'X systems, $^2J_{PC} + ^4J_{PC} = 16$ Hz, $J_{AgC} = 2.2$ Hz, $o-PC_{ph}$), 133.9 (br m, $C_{2,7}$). ^{19}F NMR ($CDCl_3$, 75.429 MHz): δ -77.7. ^{31}P NMR ($CDCl_3$, 202.46 MHz): δ 2.6 (2 d, $^1J_{107AgP} = 491$ Hz, $^1J_{109AgP} = 567$ Hz). ^{109}Ag NMR ($CDCl_3$, 23.29 MHz, Ag^+_{aq}): δ 905.4 (t, $^1J_{AgP} = 567$ Hz).

(TROPP^{Ph})Au^ICl, **19**. 250 mg (0.505 mmol) of triphenylphosphane gold(I) chloride **18** was suspended in 20 ml of toluene. After addition of 190 mg (0.505 mmol) of TROPP^{Ph} in 10 ml of toluene the solid dissolved. A few minutes later a colorless solid precipitated. It was separated by filtration and dried under vacuum. Upon adding some acetonitrile and warming the suspension up to about 40 °C the solid dissolved again. At 4 °C the product crystallized in colorless, well-designed cubes, which could be used for single crystal X-ray diffraction. Yield of $C_{27}H_{21}AuClP$ (608.82): 221 mg (71.8%); mp > 280 °C decomposes. 1H NMR (pyridine- d_5 , 200.13 MHz): δ 5.92 (d, $^2J_{PH} = 16.8$ Hz, 1H, C_{1H}), 7.00–7.35 (m, 16H, m -, p - H_{ph} and C_{8-15H} , $C_{4,5H}$), 7.81 (ddd, $^4J_{HH} = 1.7$ Hz, $^3J_{HH} = 8.2$ Hz, $^3J_{PH} = 12.0$ Hz, 4H, o - H_{ph}). ^{13}C NMR (pyridine- d_5 , 50.32 MHz): δ 56.0 (d, $^1J_{PC} = 29.6$ Hz, C_1), 128.3 (d, $^3J_{PC} = 2.5$ Hz, $C_{9,13}$), 129.0 (s, $C_{10,14}$), 129.2 (s, $C_{4,5}$), 129.3 (d, $^4J_{PC} = 1.2$ Hz, $p-C_{ph}$), 131.0 (d, $^3J_{PC} = 2.6$ Hz, $C_{11,15}$), 131.8 (d, $^2J_{PC} = 5.7$ Hz, $C_{8,12}$), 132.0 (d, $^3J_{PC} = 3.1$ Hz, $m-C_{ph}$), 133.7 (d, $^2J_{PC} = 6.3$ Hz, $o-C_{ph}$), 133.7 (d, $^3J_{PC} = 1.6$ Hz, $C_{3,6}$), 135.0 (d, $^1J_{PC} = 13.6$ Hz, PC_{ph}), 135.9 (d, $^2J_{PC} = 8.8$ Hz, $C_{2,7}$). ^{31}P NMR (pyridine- d_5 , 81.01 MHz): δ 31.2.

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