

# Synthesis and characterization of bis(triphenylphosphine)(ketone) silver and bis(triphenylphosphine)bis(ketone) silver complexes

## Crystal structure of bis(triphenylphosphine)bis(diphenylcyclopropenone) silver tetrafluoroborate

Ching-Jane Lin<sup>a</sup>, See Lin<sup>a,\*</sup>, Gene-Hsing Lee<sup>b</sup>, Yu Wang<sup>b</sup>

<sup>a</sup> Department of Chemistry, National Changhua University of Education, Changhua, Taiwan 50058, Taiwan

<sup>b</sup> Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Taiwan

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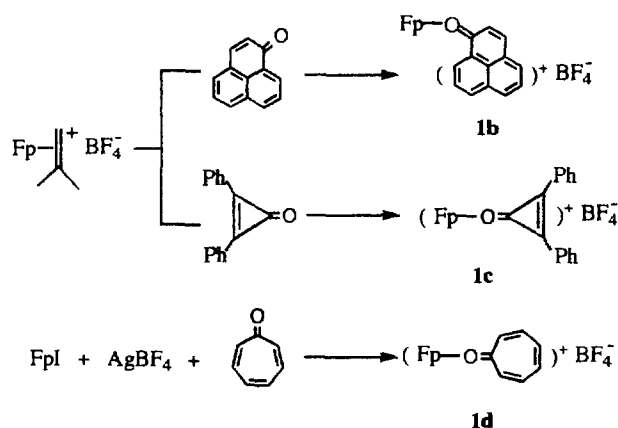
### Abstract

The bis(triphenylphosphine)silver complexes of (phenalenone) **6**, (diphenylcyclopropenone) **7**, (troponone) **8**, bis(phenalenone) **9**, bis(diphenylcyclopropenone) **10** and bis(troponone) **11** were prepared by treating bis(triphenylphosphine)silver tetrafluoroborate **5** with the respective basic ketones phenalenone **2**, diphenylcyclopropenone **3** or troponone **4** in 1 or 2 equiv. amounts. The first crystal structure of diphenylcyclopropenone adduct (complex **10**,  $(\text{Ph}_3\text{P})_2(\text{diphenylcyclopropenone})_2\text{Ag}^+\text{BF}_4^-$ ) was determined confirming the silver to oxygen  $\sigma$ -bonds. The complex **10** crystallizes in the monoclinic space group  $P2_1/c$ , with  $a = 10.419(3)\text{ \AA}$ ,  $b = 25.291(7)\text{ \AA}$ ,  $c = 20.711(4)\text{ \AA}$ ,  $\beta = 91.916(4)^\circ$ ,  $Z = 4$ ,  $V = 5454.6(24)\text{ \AA}^3$ ,  $R_F = 0.077$ ,  $R_W = 0.083$  for 7114 reflections. © 1997 Elsevier Science S.A.

### 1. Introduction

Transition metal complexes of ketones in the formation of simple adducts such as  $\text{FeCl}_3 \cdot \text{CO}(\text{C}_6\text{H}_5)_2$  and  $\text{NiBr} \cdot \text{CO}(\text{C}_6\text{H}_5)_2$  have been known for over 80 years [1]. In all of these cases, the oxygen is presumed to be bonded to the metal ions [2]. About 2 decades ago, an interest in complexes of the carbonyl function with organotransition-metal groups developed. In 1971, Silverthorn reported the iron complex **1a**, a novel iron ketone complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{dppe})(\text{OCMe}_2)$  where  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  [3]. This complex is not stable to either air or moisture, unable to be isolated. Later, Rosenblum and coworkers prepared various  $\text{Fp}(\text{carbonyl})^+$  complexes derived from simple and conjugated ketones, aldehydes, esters and amides where  $\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  [4]. In 1982, Boudjouk et al. also prepared the complexes of  $\text{Fp}(\text{carbonyl})$ , **1b–1d** [5] (Scheme 1).

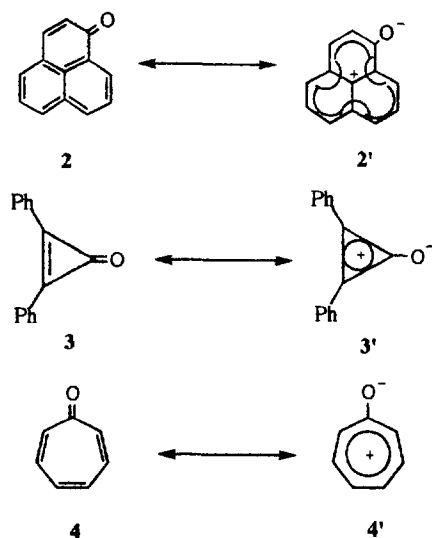
Phenalenone **2**, diphenylcyclopropenone **3** and tro-



Scheme 1.

pone **4** are typical basic ketones. The highly polar nature of the carbon–oxygen bond is due to a significant degree to the contributions of resonance forms **2'**, **3'** and **4'** [6] (Scheme 2). The resonance forms **2'**, **3'** and **4'** apparently play an important role during the reactions, favoring the rapid formation of stable oxygen–metal bonds.

\* Corresponding author. Fax: (+886) 047211190.



Scheme 2.

In the past few years, Gladysz and coworkers conducted extensive studies on rhenium complexes of aldehydes and ketones and found that the coordinated carbonyl groups are activated toward nucleophilic attack [7].

Last year we successfully prepared a series of copper(I) complexes of ketones —  $(\text{Ph}_3\text{P})_2(\text{ketone})_n\text{Cu}^+\text{BF}_4^-$  ( $n = 1, 2$ ) [8]. Recently we extended the same approach to the synthesis of  $(\text{Ph}_3\text{P})_2(\text{ketone})_n\text{Ag}^+\text{BF}_4^-$  complexes ( $n = 1, 2$ ) as reported herein.

## 2. Results and discussion

The starting material  $(\text{Ph}_3\text{P})_2\text{Ag}^+\text{BF}_4^-$  **5** was obtained from the reaction of stoichiometric amounts of

Table 1  
Comparison of carbonyl stretching frequencies

Complex	Ketone	$\nu\text{CO}$ ( $\text{cm}^{-1}$ )		
		Uncoordinated	Coordinated	$\Delta$
<b>6</b>	<b>2</b>	1644	1539	105
<b>7</b>	<b>3</b>	1626	1545	81
<b>8</b>	<b>4</b>	1582	1518	73
<b>9</b>	<b>2</b>	1644	1541	103
<b>10</b>	<b>3</b>	1626	1548	78
<b>11</b>	<b>4</b>	1582	1519	72

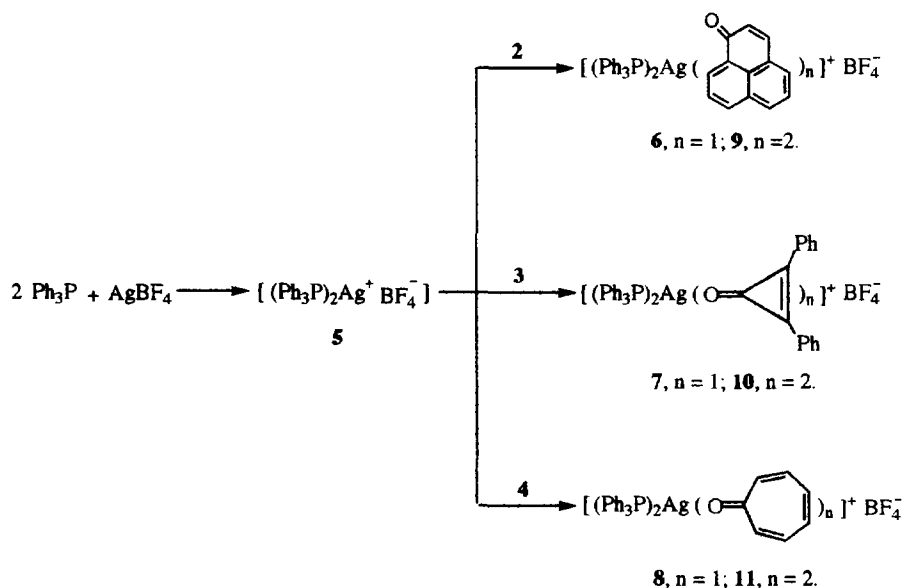
Spectra obtained in KBr pellets.

tertiary phosphine ligand with silver tetrafluoroborate in refluxing  $\text{CH}_2\text{Cl}_2$ .<sup>1</sup> The treatment of **5** with ketones **2**, **3** and **4** in 1 and 2 equiv. amounts furnished complexes **6–11** in high yields (Scheme 3).

Both bis(triphenylphosphine)(ketone)silver and bis(triphenylphosphine)bis(ketone)silver complexes are stable to air and soluble in common organic solvents such as chloroform and dichloromethane. While numerous simple metal halide adducts of **2** [10], **3** [11] and **4** [12], all presumably  $\sigma$ -bonded to oxygen, have been prepared characterized by very low solubility.

The reduction in the carbonyl stretching frequency for attachment of metal to oxygen has been reported [4–7]. As summarized in Table 1, the IR  $\nu(\text{CO})$  of complexes **6–11** are generally 72–105  $\text{cm}^{-1}$  lower than those of free ketones. The magnitudes of the  $\Delta\nu(\text{CO})$  values parallel closely those observed for complexes **1a–1c** [5]. On the other hand, the UV spectra of these complexes do not exhibit significant shifts, except com-

<sup>1</sup> We prepared  $(\text{Ph}_3\text{P})_2\text{AgBF}_4$  according the method of Mann et al. [9] using  $\text{AgBF}_4$  as starting material.



Scheme 3.

Table 2  
Comparison of ultraviolet spectra

	$\lambda_{\max}$ /nm (log $\epsilon$ ) in CH <sub>2</sub> Cl <sub>2</sub>
PNLN <sub>0</sub> 2	315 (3.58), 357 (3.99), 381 (3.93)
Complex 6	358 (3.62), 382 (3.71), 438 (3.82)
Complex 9	358 (3.61), 381 (3.73), 438 (3.84)
DPCPo 3	226 (4.28), 295 (4.43)
Complex 7	228 (4.23), 296 (4.11)
Complex 10	230 (4.28), 298 (4.22)
TROPo 4	229 (4.21), 303 (3.78)
Complex 8	230 (4.42), 302 (3.41)
Complex 11	231 (4.26), 300 (3.92)

plex 6 and complex 9. Both complex 6 and complex 9 show bathochromic shifts in the region above 300 nm (see Table 2).

The ORTEP diagram of complex 10 is given in Fig. 1. The molecular features confirm that the Ag atom is  $\sigma$ -bonded to two diphenylcyclopropenone O atoms. The crystal structure of complex 10 consists of discrete  $(\text{Ph}_3\text{P})_2\text{Ag}(\text{DPCPO})_2^+$  cations (DPCPO = diphenylcyclopropenone) and  $\text{BF}_4^-$  anions. The  $(\text{Ph}_3\text{P})_2\text{Ag}(\text{DPCPO})_2^+$  cations exhibit in the solid state a distorted tetrahedron for the central Ag coordination. The six angles around the Ag(I) center range from O1–Ag–O2 of 89.7(4)° to P1–Ag–P2 of 158.83(21)°. The O2–diphenylcyclopropenone is characterized with alternately single and double bonds for the three cyclic carbon atoms C16 to C18, whereas in the O1–diphenylcyclopropenone the fragment C1–C2–C3 is delocalized. The ketonic O angles are 128.1(20)° for Ag–O2–C16 and 139.2(12)° for Ag–O1–C1, suggesting that the ketonic O2 is more  $\text{sp}^2$ -like in bonding and O1 probably more  $\text{sp}$ -like. The Ag–P1 distance of 2.400(4) Å and the

Ag–P2 distance of 2.395(5) Å do not differ significantly from the corresponding Ag–P distances in the  $(\text{Ph}_3\text{P})_2\text{Ag}^+\text{NO}_3^-$  of 2.443(1) Å and of 2.440(1) Å [13]. The Ag–O1 distance of 2.6443(1) Å and the Ag–O2 distance of 2.471(19) Å are also quite similar to the corresponding Ag–O2 distance in the  $(\text{Ph}_3\text{P})_2\text{Ag}^+\text{NO}_3^-$  of 2.649(4) Å and of 2.464(4) Å. Furthermore, all structural parameters are pretty reasonable compared to the literature values [13–15].

### 3. Conclusion

In this work we prepared and characterized six new bis(triphenylphosphine)silver complexes of basic ketones (6–11). We also determined the first molecular structure of the complex of diphenylcyclopropenone.

### 4. Experimental section

#### 4.1. General information

All solvents were routinely purified by standard procedures and stored under nitrogen [16]. All reactions were carried out in dry solvents under oxygen-free nitrogen. Commercial reagents including diphenylcyclopropenone,  $\text{AgBF}_4$  and  $\text{Ph}_3\text{P}$  (Aldrich) were used without further purification. Phenalenone [17], tropone [18] and  $(\text{Ph}_3\text{P})_2\text{AgBF}_4$  [9] were prepared following the published methods.

Infrared spectra were recorded on a Jasco FT/IR 300 E spectrometer. <sup>1</sup>H NMR spectra were registered on a

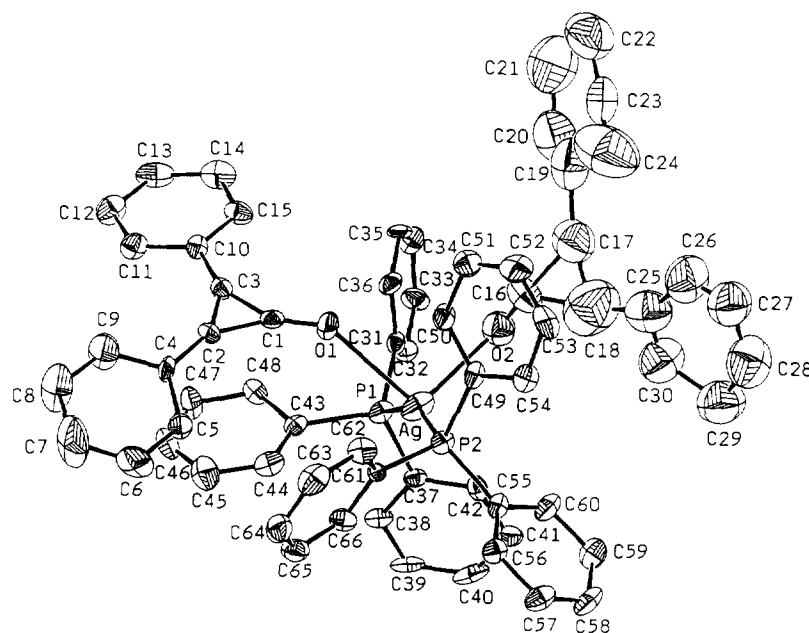


Fig. 1. Molecular structure of complex 10.

Bruker AC 400 NMR spectrometer. Ultraviolet spectra were measured on a Perkin–Elmer Lambda 5 spectrometer. Elemental analyses were done at the Analysis Center of National Cheng Kung University.

#### 4.2. X-ray crystallographic analyses for complex 10

White crystals of complex 10 were prepared by diffusion of hexane into a concentrated dichloromethane solution of complex 10 under nitrogen and at 4°C. The single crystal X-ray diffraction measurements were performed on a Nonius CAD-4 automated diffractometer using graphite monochromated Mo K $\alpha$  radiation. 25 high-angle reflections ( $15.00 < 2\theta < 21.68^\circ$ ) were used in a least squares fit to obtain accurate cell constants. The monoclinic space group  $P2_1/c$  was assigned on the basis of the systematic absences. Diffraction intensities were collected up to  $2\theta < 45^\circ$  using the  $\theta$ – $2\theta$  scan technique. The reflections with  $I_o > 2.0\sigma(I_o)$  were judged as observations and used for solution and structure refinement. Data were corrected for Lorentz-polarization factors. An empirical absorption correction based on a series of  $\Psi$  scans was applied to the data. The structure was solved by direct methods [19] and refined by a full-matrix least squares routine [20] with anisotropic thermal parameters for all non-hydrogen atoms. All of the hydrogen atoms were placed isotropically at their calculated positions and fixed in the calculations. For a summary of crystal data and refinement details, see Table 3. Selected bond distances and

Table 4  
Selected bond distances (Å) for complex 10

Ag–P1	2.400(4)
Ag–P2	2.395(5)
Ag–O1	2.623(14)
Ag–O2	2.471(19)
P1–C31	1.820(20)
P1–C37	1.823(18)
P1–C43	1.829(22)
P2–C49	1.812(19)
P2–C55	1.797(18)
P2–C61	1.792(20)
O1–C1	1.21(3)
O2–C16	1.12(3)
C1–C2	1.40(3)
C1–C3	1.41(3)
C2–C3	1.36(3)
C2–C4	1.45(3)
C3–C10	1.66(5)
C16–C17	1.54(7)
C16–C18	1.47(7)
C17–C18	1.66(6)
C17–C19	1.66(6)
C18–C25	1.61(8)

angles are listed in Tables 4 and 5. Selected atomic coordinates are listed in Table 6.

#### 4.3. Bis(triphenylphosphine)(phenalenone)silver tetrafluoroborate 6

A 100 ml Schlenk flask that had been oven-dried and purged with nitrogen was charged with  $(\text{Ph}_3\text{P})_2\text{AgBF}_4$  0.36 g (0.5 mmol), phenalenone 0.09 g (0.5 mmol) and

Table 3  
Crystallographic data and refinement details for complex 10

Empirical formula	$\text{C}_{66}\text{H}_{50}\text{O}_2\text{P}_2\text{AgBF}_4$
Formula mass (g)	1130.72
Crystal size ( $\text{mm}^3$ )	$0.03 \times 0.25 \times 0.40$
Crystal system	monoclinic
Space group	$P2_1/c$
$a$ (Å)	10.291(3)
$b$ (Å)	25.291(7)
$c$ (Å)	20.711(4)
$\beta$ (deg)	91.916(22)
$V$ (Å <sup>3</sup> )	5454.6(24)
$Z$	4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.377
$\lambda$ (Å)	0.7107
$F(000)$	2313
$\mu$ ( $\text{mm}^{-1}$ )	4.794
$2\theta$ (max)	45.0
$h; k; l$ range	–11, 11; 0, 27; 0, 22
No. of reflections	7114
No. of unique reflections	2362
No. reflections with $I > 2.0\sigma(I)$	7114
$R_F$	0.077
$R_w$	0.083
GOF	1.22

$$R_F = \frac{\sum(F_o - F_c)}{\sum(F_o)}$$

$$R_w = \left[ \frac{\sum w(F_o - F_c)}{\sum w(F_o^2)} \right]^{1/2}$$

Table 5  
Selected bond angles (deg) for complex 10

P1–Ag–P2	158.83(21)
P1–Ag–O1	91.7(3)
P1–Ag–O2	89.7(4)
P2–Ag–O1	97.8(3)
P2–Ag–O2	107.5(4)
O1–Ag–O2	98.7(6)
Ag–P1–C31	117.9(6)
Ag–P1–C37	113.0(6)
Ag–P1–C43	109.1(6)
C31–P1–C37	103.2(8)
C31–P1–C43	106.7(8)
C37–P1–C43	106.1(9)
Ag–P2–C49	109.0(6)
Ag–P2–C55	117.4(6)
Ag–P2–C61	114.6(6)
C49–P2–C55	106.5(9)
C49–P2–C61	106.3(8)
C55–P2–C61	102.2(9)
Ag–O1–C1	139.2(12)
Ag–O2–C16	128.1(20)
O1–C1–C3	152.9(20)
O1–C1–C3	149.2(20)
O2–C16–C17	166(3)
O2–C16–C18	123(4)

Table 6  
Final atomic fractional coordinates for non-H atoms of complex 10

Atom	x	y	z	$B_{iso}$
Ag	0.32252(16)	0.03009(10)	0.23148(7)	6.65(10)
P1	0.3995(5)	0.0243(3)	0.34178(21)	4.2(10)
P2	0.1849(5)	0.0165(3)	0.13802(22)	4.4(3)
O1	0.5239(13)	-0.0208(6)	0.1910(7)	6.5(8)
O2	0.4072(17)	0.1212(8)	0.2257(9)	9.8(11)
C1	0.5864(18)	-0.0598(8)	0.2045(9)	4.5(11)
C2	0.6071(17)	-0.1143(8)	0.2051(9)	4.4(11)
C3	0.6990(18)	-0.0825(8)	0.2323(8)	4.2(10)
C4	0.5630(18)	-0.1637(8)	0.1919(10)	4.8(11)
C5	0.4364(19)	-0.1761(9)	0.1790(10)	5.6(13)
C6	0.396(3)	-0.2273(12)	0.1675(14)	10.1(18)
C7	0.485(4)	-0.2683(13)	0.1711(24)	18.2(35)
C8	0.608(3)	-0.2594(13)	0.185(3)	22.2(44)
C9	0.646(3)	-0.2070(11)	0.1935(17)	11.4(21)
C10	0.8179(18)	-0.0785(8)	0.2704(8)	4.3(10)
C11	0.8789(20)	-0.1232(9)	0.2920(10)	6.1(13)
C12	0.9899(22)	-0.1185(11)	0.3323(11)	7.6(15)
C13	1.0328(22)	-0.0677(12)	0.3460(10)	7.9(15)
C14	0.9744(22)	-0.0228(11)	0.3241(10)	7.8(15)
C15	0.8636(20)	-0.0293(10)	0.2853(10)	5.9(12)
C16	0.430(3)	0.1445(12)	0.1818(14)	10.6(20)
C17	0.468(4)	0.1906(16)	0.1286(19)	16.7(32)
C18	0.336(6)	0.185(3)	0.151(3)	28.0(59)
C19	0.604(4)	0.2090(17)	0.0960(22)	18.5(34)
C20	0.696(5)	0.2176(18)	0.1423(22)	19.3(37)
C21	0.825(6)	0.2369(24)	0.119(3)	24.8(49)
C22	0.811(5)	0.2587(20)	0.042(3)	22.7(45)
C23	0.667(4)	0.2419(14)	0.0270(17)	13.7(26)
C24	0.561(7)	0.226(3)	0.020(3)	30.4(65)
C25	0.255(4)	0.2164(18)	0.0954(20)	17.4(33)
C26	0.252(4)	0.2438(19)	0.0278(21)	18.3(36)
C27	0.161(4)	0.2645(19)	0.0097(22)	19.2(37)
C28	0.051(5)	0.2657(20)	0.0403(21)	19.7(37)
C29	0.036(4)	0.2455(20)	0.1144(22)	19.2(37)
C30	0.171(4)	0.2171(19)	0.1317(20)	17.8(35)
C31	0.5333(17)	0.0665(8)	0.3672(8)	3.9(9)
C32	0.5456(17)	0.0853(8)	0.4303(9)	4.4(11)
C33	0.6467(19)	0.1154(10)	0.4493(10)	6.0(12)
C34	0.7427(19)	0.1254(9)	0.4089(11)	6.2(13)
C35	0.7360(18)	0.1051(9)	0.3473(12)	6.1(13)
C36	0.6303(18)	0.0744(9)	0.3267(9)	5.0(11)
C37	0.2768(16)	0.0242(10)	0.4961(8)	4.0(10)
C38	0.2568(17)	0.0096(9)	0.4542(8)	4.6(11)
C39	0.1668(16)	0.0242(10)	0.4961(8)	5.6(12)
C40	0.0932(19)	0.0686(11)	0.4837(10)	7.1(14)
C41	0.1091(19)	0.1000(9)	0.4280(10)	5.9(12)
C42	0.2038(18)	0.0834(8)	0.3876(9)	4.5(10)
C43	0.4487(16)	-0.0438(8)	0.3591(8)	4.1(10)
C44	0.3802(19)	-0.0852(10)	0.3315(9)	5.6(12)
C45	0.416(3)	-0.1367(10)	0.3439(11)	7.7(16)
C46	0.5204(24)	-0.1472(9)	0.3800(11)	6.8(15)
C47	0.5946(24)	-0.1090(10)	0.4045(12)	7.4(15)
C48	0.5632(19)	-0.0567(8)	0.3953(8)	4.6(11)
C49	0.2524(18)	0.0501(8)	0.0697(8)	4.3(10)
C50	0.3833(20)	0.0452(9)	0.0617(9)	5.5(12)
C51	0.4412(22)	0.0717(10)	0.0105(10)	6.6(14)
C52	0.3723(24)	0.0997(11)	-0.0314(10)	8.1(15)
C53	0.2484(25)	0.1046(10)	-0.0271(9)	7.0(15)
C54	0.1835(20)	0.0796(9)	0.0233(9)	5.6(12)
C55	0.0215(17)	0.0386(9)	0.1421(8)	4.2(10)
C56	-0.0800(18)	0.0126(9)	0.1122(9)	5.1(12)
C57	-0.2044(18)	0.0324(11)	0.1171(9)	6.6(13)

Table 6 (continued)

Atom	x	y	z	$B_{iso}$
C58	-0.2288(20)	0.0769(11)	0.1517(10)	7.1(14)
C59	-0.1230(22)	0.1044(10)	0.1798(10)	6.7(13)
C60	-0.0010(20)	0.0848(10)	0.1754(10)	6.4(13)
C61	0.1652(16)	-0.0513(7)	0.1145(8)	3.4(9)
C62	0.1844(20)	-0.0687(9)	0.0533(9)	5.6(13)
C63	0.1584(23)	-0.1211(11)	0.0391(10)	7.9(16)
C64	0.1140(23)	-0.1563(10)	0.0844(12)	7.5(16)
C65	0.0940(20)	-0.1373(10)	0.1472(10)	6.6(13)
C66	0.1224(19)	-0.0851(9)	0.1608(9)	5.3(11)
B	1.012(3)	0.2139(14)	0.3017(14)	7.9(19)
P1	1.0699(20)	0.1727(7)	0.2918(9)	14.5(14)
P2	0.8885(18)	0.2138(9)	0.2797(11)	16.2(16)
P3	0.988(3)	0.2237(8)	0.3650(9)	19.5(21)
P4	1.0496(22)	0.2589(8)	0.2785(14)	19.0(20)

$\text{CH}_2\text{Cl}_2$  (35 ml). The mixture was stirred at 40 °C for 30 min. After being cooled to room temperature, the reaction mixture was filtered and *n*-hexane added to the filtrate to precipitate a bright golden solid. The solid was collected and washed with benzene until the washings were colorless, giving analytically pure **6** (0.37 g, 82%). M.p. 181–185 °C (dec.).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.63 (d, 1H, 4Hz), 8.22 (d, 1H, 4Hz), 8.04 (d, 1H, 4Hz), 7.81–7.75 (m, 4H), 7.36–7.26 (m, 30H), 6.73 (d, 1H, 6Hz). Anal. Found: 65.04; H, 4.31.  $\text{C}_{49}\text{H}_{38}\text{AgBF}_4\text{OP}_2$  calc.: C, 65.43; H, 4.23.

#### 4.4. Bis(triphenylphosphine)(diphenylcyclopropenone)-silver tetrafluoroborate 7

This was prepared by a method similar to that described above by using  $(\text{Ph}_3\text{P})_2\text{AgBF}_4$  0.36 g (0.5 mmol), diphenylcyclopropenone 0.103 g (0.5 mmol) and  $\text{CH}_2\text{Cl}_2$  (35 ml). The mixture was stirred for 30 min at room temperature. The product was obtained as a white solid (0.38 g, 81%). M.p. 158–163 °C (dec.).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.01 (d, 2H, 4Hz), 7.97 (d, 4H, 4Hz), 7.59–7.45 (m, 4H), 7.47–7.389 (m, 30H). Anal. Found: C, 66.27; H, 4.59.  $\text{C}_{51}\text{H}_{40}\text{AgBF}_4\text{OP}_2$  calc.: C, 66.18; H, 4.33.

#### 4.5. Bis(triphenylphosphine)(tropone)silver tetrafluoroborate 8

This was prepared by a method similar to that described above by using  $(\text{Ph}_3\text{P})_2\text{AgBF}_4$  0.36 g (0.5 mmol), tropone 0.0503 g (0.5 mmol) and  $\text{CH}_2\text{Cl}_2$  (35 ml). The mixture was stirred for 30 min at room temperature. The product was obtained as a light purple solid (0.30 g, 74%). M.p. 152–157 °C (dec.).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.77–7.56 (m, 2H), 7.55–7.41 (m, 4H),

7.31–7.26 (m, 30H). Anal. Found: C, 62.36; H, 4.40.  $C_{43}H_{36}AgBF_4OP_2$  Calc.: C, 62.57; H, 4.37.

#### 4.6. Bis(triphenylphosphine)bis(phenalenone)silver tetrafluoroborate **9**

This was prepared by a method similar to that described above by using  $(Ph_3P)_2AgBF_4$  0.36 g (0.5 mmol), phenalenone 0.180 g (1.0 mmol) and  $CH_2Cl_2$  (35 ml). The mixture was stirred for 30 min at 40 °C. The product was obtained as an orange-yellow solid (0.46 g, 85%). M.p. 156–160 °C (dec.).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  8.58 (d, 2H, 6 Hz), 8.20 (d, 2H, 8 Hz), 8.02 (d, 2H, 8 Hz), 7.77–7.62 (m, 8H), 7.40–7.26 (m, 30H), 6.68 (d, 2H, 10 Hz). Anal. Found: C, 68.62; H, 4.36.  $C_{62}AgBF_4O_2P_2$  calc.: C, 68.98; H, 4.27.

#### 4.7. Bis(triphenylphosphine)bis(diphenylcyclopropenone)silver tetrafluoroborate **10**

This was prepared by a method similar to that described above by using  $AgBF_4$  0.36 g (0.5 mmol), diphenylcyclopropenone 0.206 g (1.0 mmol) and  $CH_2Cl_2$  (35 ml). The mixture was stirred for 30 min at room temperature. The product was obtained as a white solid (0.46 g, 82%). M.p. 112–116 °C.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  8.01–7.71 (m, 20H), 7.46–7.37 (m, 30H). Anal. Found: C, 70.51; H, 4.80.  $C_{66}H_{50}AgBF_4O_2P_2$  calc.: C, 70.08; H, 4.42.

#### 4.8. Bis(triphenylphosphine)bis(tropone)silver tetrafluoroborate **11**

This was prepared by a method similar to that described above by using  $AgBF_4$  0.36 g (0.5 mmol), tropone 0.106 g (1.0 mmol) and  $CH_2Cl_2$  (35 ml). The mixture was stirred for 30 min at room temperature. The product was obtained as a light brown solid (0.33 g, 72%). M.p. 104–108 °C.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.69–7.55 (m, 12H), 7.41–7.23 (m, 30H). Anal. Found: C, 64.66; H, 4.63.  $C_{50}H_{42}AgBF_4O_2P_2$  calc.: C, 64.47; H, 4.51.

### 5. Supplementary material

Complete bond distances, bond angles, atomic coordinates, anisotropic thermal parameters, torsion angles and plane calculations for complex **11** are available. Ordering information is given on any current masthead page.

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