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Ylide-Metal Complexes. VIII.[1] The Preparation and Properties of Metal (Cu, Ag, Au, Zn, Cd, Hg, Ge, Sn, Pb, Pd, and Pt) Complexes with Methylenetris(dimethylamino)phosphorane

Yoshihisa YAMAMOTO
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02

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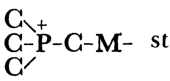
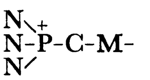
Bis[methylenetris(dimethylamino)phosphorane]metal chlorides, $[(Me_2N)_3PCH_2\text{-}M\text{-}CH_2P(NMe_2)_3]Cl_n$ (M: Cu, Ag, Au, Zn, Cd, Hg; *n*: 1 or 2), have been isolated from a reaction mixture of methylenetris(dimethylamino)phosphorane $(Me_2N)_3P{=}CH_2$ (**L**) and CuCl, AgCl, $(C_6H_5)_3PAuCl$, $ZnCl_2$, $CdCl_2$, or $HgCl_2$ in the mole ratio of 2:1 or 3:1. The reactions of **L** with R_3MCl (M: Sn, Pb; R: Me, C_6H_5) in the mole ratio 1:1 yield new monomeric compounds of [methylenetris(dimethylamino)phosphorane]trimethyl(or triphenyl)-metal chloride, $[(Me_2N)_3PCH_2\text{-}MR_3]Cl$. The reactions of **L** with $PdCl_2$ or PtI_4 in the mole ratio of 2:1 or 4:1 yield $[(Me_2N)_3PCH_2]_2PdCl_2$ and $[(Me_2N)_3PCH_2]_4PtI_4$, respectively. The Ag, Au, Sn, and Pb complexes are stable. Their properties are compared with those of the metal complexes with methylenetriphenylphosphorane, $(C_6H_5)_3P{=}CH_2$.

Many investigations of the metal complexes[2-4] with phosphonium ylides, *e.g.*, with methylenetrimethyl- or methylenetriphenylphosphorane, have been reported. Their complexes have the  $\overset{C\diagdown +}{\underset{C\diagup}{C\text{-}P\text{-}C\text{-}M\text{-}}}$ structure. However, few investigations of the ylide-metal complexes which have the  $\overset{N\diagdown +}{\underset{N\diagup}{N\text{-}P\text{-}C\text{-}M\text{-}}}$ structure have been described: only the nitridobis(methylenedimethylphosphorane)metal complexes[5] and bis[methylenetris(dimethylamino)phosphorane]gold chloride.[6]

The present paper deals with the preparation and properties of group IB, IIB, IVA, and VIII metal complexes with methylenetris(dimethylamino)phosphorane, $(Me_2N)_3P{=}CH_2$ (**L**). Their properties are compared with those of the metal complexes,[4,7-9] with methylenetriphenylphosphorane, $(C_6H_5)_3P{=}CH_2$. In the previous paper[2] of this series, we have reported the preparation and properties of group IIA (Be, Mg) and IIIA (Al, Ga, In) complexes with methylenetriphenylphosphorane.

Results and Discussion

Bis[methylenetris(dimethylamino)phosphorane]group IB and IIB metal complexes (**1—6**) have been isolated from a reaction mixture of methylenetris(dimethylamino)phosphorane (**L**) and CuCl, AgCl, $(C_6H_5)_3PAuCl$, $ZnCl_2$, $CdCl_2$, or $HgCl_2$ in the mole ratio of 2:1 or 3:1. Complex **2** is stable in dichloromethane, though unstable in chloroform, and is sensitive to light.

$$\underset{\substack{\mathbf{L}\\ m:\ 2\text{ or }3}}{m(Me_2N)_3P{=}CH_2} + \underset{n:\ 1\text{ or }2}{MCl_n} \longrightarrow$$

$$\underset{\mathbf{1—6}}{[(Me_2N)_3PCH_2\text{-}M\text{-}CH_2P(NMe_2)_3]Cl_n}$$

No.	1	2	3	4	5	6
M	Cu	Ag	Au	Zn	Cd	Hg

Complex **3**[6] is highly hygroscopic. It is soluble in water and organic solvents, and is stable in air and solution.

The ^1H NMR spectra of **2** and **3** showed a doublet signal for the methylene group at 1.3 ppm for **2** (0.99 ppm for **3**) and a doublet signal for the methyl group at 2.6 ppm in a ratio of 4:36 at room temperature (r.t.) in dichloromethane-d_2. The chemical shifts of the methylene group are at a lower field than that[10] (0.1 ppm) of **L**. In the ^{13}C NMR spectra of **2** and **3**, the chemical shifts (+9 ppm) of the methylene carbon are at a lower field than that (−9 ppm) of **L**. Their coupling constants ($^1J_{CP}$: 97 for **2** and 89 Hz for **3**) are much smaller than that (176 Hz) of **L**. These spectral properties are similar to those[4,7,8] of bis(methylenetriphenylphosphorane)metal chloride, $[(C_6H_5)_3P\overset{R}{\overset{|}{C}}H\text{-}M\text{-}\underset{CHP(C_6H_5)_3]Cl_n}{\overset{R}{\overset{|}{\ }}}$ (**7**) (M: group IB and IIB; R: H; *n*: 1, 2). Thus, the ylide is bonded to the metal atom through the carbanionic donor atom.

The following differences between **3** and **7** (M: Au; R: H) are significant: i) the chemical shift (δCH_2P) of **3** is at a higher field than that[7] of **7** as shown in Fig. 1; ii) the coupling constant ($^2J_{HCP}$) of **3** is similar to that of **L**, but that[7] (14 Hz) of **7** is larger than that[11] (7.5 Hz) of methylenetriphenylphosphorane, $(C_6H_5)_3P{=}CH_2$ (**L′**); iii) the coupling constant (J_{CP}) of **3** is much larger than that[7] (39 Hz) of **7**. The coupling constants ($^3J_{HCNP}$, $^2J_{CNP}$) and chemical shifts ($\delta PNCH_3$) of the methyl groups in **2** and **3** are similar to those of **L**, as shown in Table 1. Complexes **1** and **4—6** are unstable in dichloromethane and chloroform at r.t.; they give a methyltris(dimethylamino)phosphonium chloride, $[(Me_2N)_3PCH_3]Cl$ (**8**).

[Methylenetris(dimethylamino)phosphorane]silver chloride (**9**) and the corresponding zinc dichloride (**10**) have been prepared from the reaction mixture of **L** with AgCl or $ZnCl_2$ in the mole ratio of 1:1. Complexes **9** and **10** are also unstable in dichloromethane and chloroform at r.t.; they give the corresponding phosphonium chloride (**8**). Though their structures are un-

TABLE 1. ^{1}H AND ^{13}C NMR DATA OF COMPLEXES, YLIDE AND RELATED COMPOUNDS

^{1}H Complex No.	$CH_{2(3)}P$ δ	$CH_{2(3)}P$ $^2J_{HCP}$/Hz	NCH_3 δ	NCH_3 $^3J_{HCNP}$/Hz	C_6H_5 δ	CH_3 δ	Solvent and Standard	
2	1.32 d(4H)	14.5	2.63 d(36H)	9.8			CD_2Cl_2	1)
3	0.99 d(4H)	13.5	2.68 d(36H)	9.8			D_2O	2)
11	1.94 d(2H)	13.7	2.70 d(18H)	9.3		0.69 s(9H)	CD_2Cl_2	1)
12	1.68 d(2H)	14.0	2.50 d(18H)	9.8	7.2—8.2 m(15H)		CD_2Cl_2	1)
13	1.64 d(2H)	14.0	2.52 d(18H)	9.8	7.2—8.2 m(15H)		CD_2Cl_2	1)
8	1.9 d(3H)	14.0	2.68 d(18H)	9.8			D_2O	2)
	2.25 d(3H)	14.0	2.77 d(18H)	10.0			CD_2Cl_2	1)
L	0.1 d(2H)	13.0	2.45 d(18H)	10.0			C_6D_6	1)
L'	0.76 d(2H)	7.5			6.9—8.0 m(15H)		C_6D_6	1)
L'*	0.13 d(2H)	7.5			6.1—7.2 m(15H)		C_6D_6	3)
^{13}C	$CH_{2(3)}P$ δ	$CH_{2(3)}P$ $^1J_{CP}$/Hz	NCH_3 δ	NCH_3 $^2J_{CNP}$/Hz				
2	9.13 d	96.6	36.7 d	3.9			CD_2Cl_2	4)
3	9.48 d	88.9	37.4 d	2.0			D_2O	5)
	7.9 d	87.9	37.2 d	2.93			$CDCl_3$	6)
8	11.2 d	113.3	36.6 d	3.9			D_2O	5)
	9.04 d	112.3	36.6 d	3.9			$CDCl_3$	6)
L	−9.15 d	175.8	37.0 d	2.93			C_6D_6	7)

Standard: 1) internal TMS, 2) internal DSS, 3) external TMS, 4) CD_2Cl_2 (δ=53.6), 5) dioxane (δ=67.4), 6) $CDCl_3$(δ=77.1), 7) C_6D_6 (δ=128). *: Ref. 11.

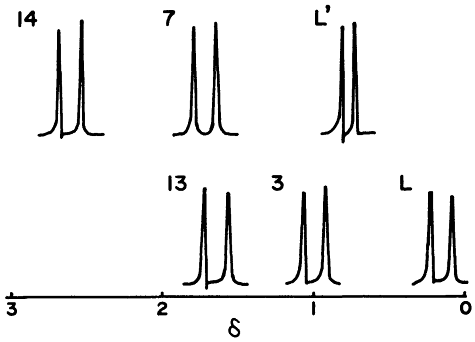


Fig. 1. ^{1}H NMR spectra of ylides **L**, **L'** and complexes **3**, **7**, **13**, **14**.
L: $(Me_2N)_3P{=}CH_2$ in C_6D_6, **L'**: $(C_6H_5)_3P{=}CH_2$ in C_6D_6, **3**: $[(Me_2N)_3PCH_2\text{-}Au\text{-}CH_2P(NMe_2)_3]Cl$ in CD_2Cl_2, **7**: $[(C_6H_5)_3PCH_2\text{-}Au\text{-}CH_2P(C_6H_5)_3]Cl$ in CD_2Cl_2, **13**: $[(Me_2N)_3PCH_2\text{-}Pb(C_6H_5)_3]Cl$ in CD_2Cl_2, **14**: $[(C_6H_5)_3PCH_2\text{-}Pb(C_6H_5)_3]Cl$ in CD_2Cl_2.

$$m(Me_2N)_3P{=}CH_2 + mMCl_n \longrightarrow \underset{\textbf{9, 10}}{[(Me_2N)_3PCH_2\text{-}MCl_n]_m}$$

n: 1 or 2

No.	**9**	**10**
M	Ag	Zn

certain, they should not be polymers because they are soluble in dichloromethane. The elemental analyses of **9** and **10** agree with that of $[(Me_2N)_3PCH_2\text{-}MCl_n]_m$ (n: 1 or 2). Thus they can be a oligomer.[4a)]

[Methylenetris(dimethylamino)phosphorane]triphenyltin chloride (**11**) and [methylenetris(dimethylamino)phosphorane]triphenyltin (**12**) or -lead (**13**) chloride have been isolated from the reaction mixture of **L** and trimethyltin chloride or triphenyltin (or lead) chloride. They are stable in dichloromethane and air at r.t. The ^{1}H NMR spectra of **11**—**13** showed the doublet signals for the methylene group at 1.6—1.9 ppm and the doublet signals for the methyl group ($PNCH_3$) at 2.5—2.7 ppm in a ratio of 2:18 at r.t. in dichloromethane-d_2. The methyl protons (MCH_3) of **11** and the phenyl protons of **12** and **13** are assigned to a singlet signal at 0.69 ppm (9H) and the multiplet signals at 7.2—8.2 ppm (15H), respectively. The chemical shifts of the methylene group of **11**—**13** are at a lower field than that of **L**. This is similar to that[9)] of (methylenetriphenylphosphorane)triphenyllead chloride, $[(C_6H_5)_3PCH_2\text{-}MPh_3]Cl$ (**14**) M: Pb. The chemical shift of the methylene group of **12** is at a higher field than that of **11**. This difference is ascribed to the methyl (MCH_3) and phenyl groups. The chemical shift (δCH_2-P) of **13** is at a higher field than that[9)] of **14** (M: Pb), as shown in Fig. 1.

$$(Me_2N)_3P{=}CH_2 + R_3MCl \longrightarrow \underset{\textbf{11—13}}{[(Me_2N)_3PCH_2\text{-}MR_3]Cl}$$

No.	**11**	**12**	**13**
M	Sn	Sn	Pb
R	Me	Ph	Ph

Tetrakis[methylenetris(dimethylamino)phosphorane]germanium tetrachloride (**15**), tris[methylenetris(dimethylamino)phosphorane]tin dichloride (**16**), bis[methylenetris(dimethylamino)phosphorane]lead dichloride (**17**), bis[methylenetris(dimethylamino)phosphorane]paradium dichloride (**18**) and tetrakis[methylenetris(dimethylamino)phosphorane]platinum tetraiodide (**19**) have been isolated from the reaction mixture of **L** and $GeCl_4$, $SnCl_2$, $PbCl_2$, $PdCl_2$, or PtI_4. They are unstable in dichloromethane or chloroform at r.t., and give the corresponding phosphonium salt (**8**). Complexes **17** and **19** are stable in air. The melting points or decomposition temperatures of both the complexes differ from those of the ylide and **8**. They are thermally stable in the solid state. These properties resemble those[4,7,8] of **7** (M: group IB, IIB metal; R: Me, *i*-Pr) and **14**[9] (M: Ge, Sn). Thus, the ylide seems to be bonded to the metal atom in the solid state,[9] though the structures are uncertain. Complexes **16** and **17** are not so stable as complexes **11**—**13** in dichloromethane. This property is similar to those[9] of other lead complexes such as $[Ph_3PCH_2PbPh_3]Cl$ and $[Ph_3PCH_2]_2PbCl_2$.

$$m(Me_2N)_3P{=}CH_2 + MCl_n \longrightarrow [(Me_2N)_3PCH_2]_mMCl_n \quad \textbf{15—18} \qquad n\text{: } 2, 4$$

$$m(Me_2N)_3P{=}CH_2 \xrightarrow{PtI_4} [(Me_2N)_3PCH_2]_4PtI_4 \quad \textbf{19}$$

No.	**15**	**16**	**17**	**18**
M	Ge	Sn	Pb	Pd
m	4	3	2	2
n	4	2	2	2

In the complexes of the methylenetris(dimethylamino)phosphorane and methylenetriphenylphosphorane, the most remarkable difference between them is solubility in water: *i.e.*, the gold complex (**3**) is soluble but complex (**7**) is insoluble.

The feature of the stable metal complexes with methylenetris(dimethylamino)phosphorane and alkylidenetriphenylphosphorane is ascribed to three factors of metals, ylides, and structures as follows. i) Metals: the metals of stable complexes are Cu(I), Ag(I), Au(I), Zn(II), Cd(II), Be(II), Mg(II), Al(III), Ga(III), In(III), Sn(IV), and Pb(IV). ii) Ylides: *e.g.*, the zinc complex with methylenetriphenylphosphorane is stable, though the complex with methylenetris(dimethylamino)phosphorane is unstable. iii) Structures: the silver complex (**2**) with the composition ratio 2:1 is stable, though the complex (**7**) with the composition ratio 1:1 is unstable; the tin and lead complexes (**11** and **13**) with the coexisting methyl and phenyl ligands are stable, though those complexes (**16** and **17**) with the coexisting chloride ion are unstable.

Experimental

Measurements. The NMR spectra were recorded with an R-40 spectrometer (Hitachi) for ^1H NMR and an FX-60 (JEOL) for ^{13}C NMR.

Starting Materials. Methylenetris(dimethylamino)phosphorane (**L**) was prepared from methyltris(dimethylamino)phosphonium bromide and sodium in liquid ammonia by Issleib's method.[12] Methyltris(dimethylamino)phosphonium bromide was prepared from the reaction mixture of tris(dimethylamino)phosphine[13] and methyl bromide.

Ylide-Metal Complexes. *Bis[methylenetris(dimethylamino)phosphorane]copper Chloride (1)*: The ylide of 0.22 g (1.24 mmol) was added to dry THF (10 cm^3) under nitrogen. To the solution was added CuCl of 0.045 g (0.455 mmol). The mixture was stirred for 1 d at room temperature. The white complex which formed was filtered and dried under vacuum. Yield: 0.15 g (72.8%). Found: C, 36.73; H, 9.07%. Calcd for $C_{14}H_{40}N_6P_2CuCl$ (MW 453.46) C, 37.08; H, 8.89%.

Bis[methylenetris(dimethylamino)phosphorane]silver Chloride (2): The ylide of 0.56 g (3.16 mmol) was added to dry THF (5 cm^3) under nitrogen. To the solution was added AgCl (0.15 g, 1.05 mmol). The mixture was stirred for 1 d at r.t. The white complex which formed was filtered and dried under vacuum. Yield: 0.40 g (76.8%). Found: C, 34.02; H, 8.08%. Calcd for $C_{14}H_{40}N_6P_2AgCl$ (MW 497.78) C, 33.78; H, 8.10%.

Bis[methylenetris(dimethylamino)phosphorane]gold Chloride (3): Triphenylphosphinegold chloride of 0.36 g (0.727 mmol) and ylide of 0.39 g (2.2 mmol) were added to dry benzene of 20 cm^3 under nitrogen. The mixture was stirred for approximately 1 d at room temperature. The white complex which precipitated was filtered, washed with dry benzene and dried under vacuum. Yield: 0.33 g (77.3%). Found: C, 29.00; H, 6.86%. Calcd for $C_{14}H_{40}N_6P_2AuCl$ (MW 586.88) C, 28.65; H, 6.87%.

Bis[methylenetris(dimethylamino)phosphorane]zinc Dichloride (4): Zinc chloride of 0.15 g (1.10 mmol) was added to the dry THF (20 cm^3) solution of ylide (0.40 g, 2.26 mmol). The mixture was stirred at r.t. under nitrogen. After 1 d, the solution was filtered and ether was added to the filtrate at −60 °C. The white complex which formed was filtered and dried. Yield: 0.11 g (20.4%). Found: C, 33.62; H, 8.38%. Calcd for $C_{14}H_{40}N_6P_2ZnCl_2$ (MW 490.74) C, 34.26; H, 8.22%.

Bis[methylenetris(dimethylamino)phosphorane]cadmium Dichloride (5): Cadmium chloride of 0.17 g (0.93 mmol) was added to the dry THF (20 cm^3) solution of ylide (0.51 g, 2.88 mmol). The mixture was stirred for 3 d. Pentane was added to the solution and the resulting white precipitated complex was filtered and dried. Yield: 0.1 g (20.1%). Found: C, 31.48; H, 7.29%. Calcd for $C_{14}H_{40}N_6P_2CdCl_2$ (MW 537.76) C, 31.27; H, 7.50%.

Bis[methylenetris(dimethylamino)phosphorane]mercury Dichloride (6): Mercury(II) chloride of 0.2 g (0.74 mmol) was added to the dry THF (9 cm^3) solution of ylide of 0.34 g (1.92 mmol) and the mixture was stirred for 3 d. The white precipitated complex was filtered, washed with dry pentane and dried under vacuum. Yield: 0.43 g (93.3%). Found: C, 27.10; H, 6.21%. Calcd for $C_{14}H_{40}N_6P_2HgCl_2$ (MW 625.95) C, 26.86; H, 6.44%. This complex is hygroscopic. Decomp 188 °C under nitrogen.

[Methylenetris(dimethylamino)phosphorane]silver Chloride (9): Silver chloride of 0.17 g (1.19 mmol) was added to the dry THF solution (5 cm^3) of ylide 0.23 g (1.30 mmol) and the mixture was stirred for 16 h under nitrogen at r.t. The white complex which formed was filtered and dried under vacuum. Yield: 0.31 g (81.5%). Found: C, 26.40; H, 6.75%. Calcd for $C_7H_{20}N_3PAgCl$ (MW 320.55) C, 26.23; H, 6.29%. Complex **9** was sensitive to light.

[Methylenetris(dimethylamino)phosphorane]zinc Dichloride (10): Zinc chloride of 0.15 g (1.10 mmol) was added to the dry THF (8 cm^3) solution of ylide (0.20 g, 1.13 mmol) and the mixture was stirred 1 d under nitrogen. Ether was added to the solution and the white complex which precipitated was filtered and dried under vacuum. Yield: 0.15 g (43.5%). Found: C, 26.73; H, 6.43%. Calcd for $C_7H_{20}N_3PZnCl_2$ (MW 313.51) C, 26.82; H, 6.43%.

[Methylenetris(dimethylamino)phosphorane]trimethyltin Chloride (11): Trimethyltin chloride of 0.53 g (2.66 mmol) was added to the dry THF (7 cm^3) solution of ylide of 0.48 g (2.71 mmol) at 0 °C. The mixture was stirred for 1 d at r.t. The white complex which precipitated was filtered, washed with pentane and dried. Yield: 0.5 g (50.0%). Found: C, 30.93; H, 7.57%. Calcd for $C_{10}H_{29}N_3PSnCl$ (MW 376.48) C, 31.90; H,

7.76%. Mp 215—218 °C.

[Methylenetris(dimethylamino)phosphorane]triphenyltin Chloride (12): The ylide (0.10 g, 0.56 mmol) and triphenyltin chloride (0.21 g, 0.54 mmol) were added to dry THF (10 cm^3) and the resulting mixture was stirred 1 d at 0 °C. The white complex which precipitated was filtered and washed with pentane of 10 cm^3. Yield: 0.16 g (52.2%). Found: C, 52.94; H, 6.70%. Calcd for $C_{25}H_{35}N_3PSnCl$ (MW 562.69) C, 53.36; H, 6.27%. Mp 267—270 °C.

[Methylenetris(dimethylamino)phosphorane]triphenyllead Chloride (13): The mixture of the ylide (0.34 g, 1.92 mmol) and triphenyllead chloride (0.89 g, 1.88 mmol) in dry THF (8 cm^3) were stirred for 1 d at r.t. The white precipitate was filtered, washed with pentane and dried. Yield: 0.55 g (45.0%). Found: C, 46.40; H, 5.87%. Calcd for $C_{25}H_{35}N_3PPbCl$ (MW 651.12) C, 46.12; H, 5.42%. Mp 258—261 °C.

Tetrakis[methylenetris(dimethylamino)phosphorane]germanium Tetrachloride (15): Germanium tetrachloride (0.051 g, 0.24 mmol) was added to the dry THF (8 cm^3) solution of ylide of 0.17 g (0.96 mmol) at 0 °C, and the mixture was stirred 1 d at r.t. The white complex which precipitated was filtered and dried under vacuum. Yield: 0.14 g (63.7%). Found: C, 35.79; H, 8.89%. Calcd for $C_{28}H_{80}N_{12}P_4GeCl$ (MW 923.32) C, 36.42; H. 8.73%.

Tris[methylenetris(dimethylamino)phosphorane]tin Dichloride (16): Tin(II) chloride of 0.14 g (0.73 mmol) was added to the dry THF (8 cm^3) solution of ylide (0.4 g, 2.26 mmol). The mixture was stirred for 3 d at r.t. The white precipitate was filtered, washed with dry pentane and dried. Yield: 0.23 g (60.5%). Found: C, 34.80; H, 8.15%. Calcd for $C_{21}H_{60}N_9P_3SnCl_2$ (MW 721.28) C, 34.97; H, 8.38%.

Bis[methylenetris(dimethylamino)phosphorane]lead Dichloride (17): To the dry THF (18 cm^3) solution of ylide of 0.27 g (1.52 mmol) was added $PbCl_2$ (0.21 g, 0.76 mmol) at 0 °C and the mixture was stirred 1 d at r.t. The white complex which formed was filtered and dried. Yield: 0.36 g (75.0%). Found: C, 25.86; H, 6.18%. Calcd for $C_{14}H_{40}N_6P_2PbCl_2$ (MW 632.48) C, 26.59; H, 6.37%. Decomp 248 °C.

Bis[methylenetris(dimethylamino)phosphorane]paradium Dichloride (18): To the dry THF (12 cm^3) solution of ylide of 0.46 g (2.60 mmol) was added $PdCl_2$ (0.18 g, 1.02 mmol) at r.t. and the mixture was stirred 1 d. The precipitated complex was filtered, washed with pentane and dried. Yield: 0.42 g (77.8%). Found: C, 32.00; H, 8.06%. Calcd for $C_{14}H_{40}N_6P_2PdCl_2$ (MW 531.76) C, 31.62; H, 7.58%.

Tetrakis[methylenetris(dimethylamino)phosphorane]platinum Tetraiodide (19): Platinum(IV) iodide of 0.30 g (0.43 mmol) was added to the dry THF (10 cm^3) solution of ylide (0.35 g, 1.97 mmol) and the mixture was stirred 1 d at r.t. The yellow precipitate which formed was filtered, washed with dry ether and dried. Yield: 0.46 g (75.8%). Found: C, 24.23; H, 6.15%. Calcd for $C_{28}H_{80}N_{12}P_4PtI_4$ (MW 1411.62) C, 23.82; H, 5.71%. Mp 189—191 °C.

All complexes are soluble in dichloromethane and chloroform. Complexes **2**, **3**, **6**, **11**, and **16** are soluble in water and organic solvents such as acetone, alcohols, DMF, and DMSO. Complexes **12** and **13** are soluble in the organic solvents and insoluble in water. Complex **17** is slightly soluble in dichloromethane-chloroform (1 : 1) and insoluble in water and the organic solvents. Complex **19** is soluble in DMSO and MeOH, but insoluble in water, acetone, and DMF.

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