slowly in chloroform, while (dmphen)(methyl acrylate)platinum undergoes oxidative addition of $CHCl_3$ within a few hours. The NMR data of some (*N*,*N*-chelate)(olefin)platinum(0) complexes have been reported.[6]

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# 28. DIMETHYLPALLADIUM(II) AND MONOMETHYLPALLADIUM(II) REAGENTS AND COMPLEXES


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The displacement of a weak ligand by a stronger donor ligand is a widely used strategy in the synthesis of organometallic complexes. This strategy is


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ideal when the labile reagent complex is stable in air in the solid state at convenient temperatures. Several suitable organopalladium(II) reagents have been developed recently, in particular [$PdMe_2$(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[1,2] and [$PdMe_2$(pyridazine)]$_n$[3,4] for the synthesis of complexes of 2,2′-bipyridyl (bpy), tertiary phosphines, and 1,4,7-trithiacyclononane. The reagents PdIMe(tmeda)[5] and [$PdMe(SMe_2)(\mu$-X)]$_2$ (X = Cl, Br, I)[3,4,6–9] are also being used for the synthesis of a wide range of monomethylpalladium(II) complexes. The dimethylpalladium(II) reagents may also be used for the synthesis of a wide range of monomethylpalladium(II) complexes. The dimethylpalladium(II) reagents may also be used for the synthesis of organopalladium(IV) complexes.[1,7,10–16]

The synthesis of the tmeda, pyridazine, and dimethylsulfide complexes is described here, followed by representative syntheses of bpy, $PPh_3$, and bis(diphenylphosphino)ferrocene (dppf) complexes. Anaerobic techniques are used for organolithium and oxidative addition reactions, and are recommended, although not essential, for the subsequent ligand-exchange reactions. Products were stored at ambient temperature, preferably under nitrogen, except for $PdMe_2$(tmeda), $PdMe_2$(pyridazine), and [$PdMe(SMe_2)$-$(\mu$-X)]$_2$ (X = Cl, Br, I), which were stored at $-20°C$.

## A. *TRANS*-DICHLOROBIS(DIMETHYLSULFIDE)PALLADIUM(II)

$$PdCl_2 + 2SMe_2 \rightarrow \textit{trans}\text{-}[PdCl_2(SMe_2)_2]$$

■ **Caution.** *Dimethylsulfide is toxic and has an unpleasant odor. The synthesis must be carried out in a well-ventilated hood.*

Dimethylsulfide (0.40 mL, 10.5 mmol) is added at ambient temperature to a magnetically stirred suspension of $PdCl_2$ (0.46 g, 4.3 mmol) in dichloromethane (30 mL) under a nitrogen atmosphere in a 100-mL, round-bottomed flask. The suspension is stirred for 1 h, giving a clear orange solution. The solvent and the excess of dimethylsulfide are evaporated in a vacuum, the resulting orange solid is redissolved in dichloromethane (15 mL) and filtered through filter-aid (Celite). The filter was rinsed with dichloromethane (2 × 10 mL). The combined fractions were collected in a 50-mL, round-bottomed flask and evaporated to dryness in a vacuum to give a microcrystalline, orange solid. The yield is 0.74 g (100%). $^1$H NMR in $CDCl_3$: $\delta$ 2.39 (s, $SMe_2$). $^{13}$C NMR in $CDCl_3$: $\delta$ 22.93 (s, $SMe_2$).

*Anal.* Calcd. for C, 15.9; H, 4.0. Found: C, 15.9; H, 4.0.

*Properties*

The orange solid may be stored at ambient temperature and is soluble in a range of organic solvents.

## B. *TRANS*-DIBROMOBIS(DIMETHYLSULFIDE)PALLADIUM(II)

$$trans\text{-}[PdCl_2(SMe_2)_2] + 2KBr \rightarrow trans\text{-}[PdBr_2(SMe_2)_2] + 2KCl$$

Potassium bromide (0.60 g, 5.0 mmol) in water (2 mL) is added at ambient temperature to a magnetically stirred orange solution of *trans*-$[PdCl_2(SMe_2)_2]$ (0.50 g, 1.66 mmol) in acetone (15 mL) in a 50-mL, round-bottomed flask. A yellow precipitate and red solution formed immediately, and after stirring for 1 h the solvent is evaporated in a vacuum. The red-orange residue is extracted with benzene ($2 \times 2$ mL) and the suspension filtered through filter aid (Celite) to remove a yellow-brown solid. The volume of the filtrate is reduced to 5 mL in a vacuum and petroleum ether (10 mL, bp 60–80°C) is added to precipitate the product as a red-orange solid (0.55 g, 85%). $^1$H NMR in $CDCl_3$: $\delta$ 2.53 (s, $SMe_2$). $^{13}$C NMR in $CDCl_3$: $\delta$ 24.3 (s, $SMe_2$).

*Anal.* Calcd. for C, 12.3; H, 3.1; S, 16.4. Found: C, 12.5; H, 3.2; S, 16.6.

*Properties*

The red-orange solid may be stored at ambient temperature and is soluble in a range of organic solvents.

## C. DIMETHYL(PYRIDAZINE)PALLADIUM(II)

$$trans\text{-}[PdCl_2(SMe_2)_2] + 2LiMe + C_4H_4N_2 \rightarrow 1/n[PdMe_2(C_4H_4N_2)]_n + 2LiCl + 2SMe_2$$

■ **Caution.** *Solutions of LiMe are flammable, and $SMe_2$ is toxic and has an unpleasant odor.*

Methyllithium (0.4% LiCl; 3.33 mL, 3.50 mmol) is added to a cooled (−78°C) and stirred suspension of *trans*-$[PdCl_2(SMe_2)_2]$ (0.50 g, 1.67 mmol) in anhydrous diethyl ether (100 mL) under a nitrogen atmosphere in a three-necked, 250-mL, round-bottomed flask fitted with a nitrogen inlet, pressure-equalizing dropping funnel, and a septum. The suspension is stirred for 1 h at

– 78°C, followed by stirring at ca. – 40°C until a clear, colorless solution is obtained free from unreacted *trans*-$[PdCl_2(SMe_2)_2]$. Pyridazine* (1,2-diazine) (0.13 mL, 1.81 mmol) in anhydrous diethyl ether (10 mL) is added dropwise to yield a yellow-orange precipitate, followed by water (2 mL) at – 10°C and rapid filtration in air on a sintered glass filter. This solid is washed with several portions of water (3 × 10 mL) and diethyl ether (4 × 10 mL) and dried immediately under high vacuum at ambient temperature. The yield is 0.26 g (72%). $^1$H NMR in $(CD_3)_2CO$: $\delta$ 9.23 m (H3, 6), 7.98 m (H4,5), 0.06 s (PdMe).

*Properties*

The yellow solid may be stored at – 20°C; it slowly darkens over a period of weeks but is still useful in syntheses. The complex is soluble in a range of organic solvents and pyridazine/ligand exchange reactions have been satisfactorily accomplished in acetone, benzene, dichloromethane, and chloroform, but solutions of the complex are unstable in the absence of added ligand.

## D. DIMETHYLBIS(DIMETHYLSULFIDE)DI($\mu$-CHLORO)-DIPALLADIUM(II)

*trans*-$[PdCl_2(SMe_2)_2]$ + LiMe →

$$1/2\,[PdMe(SMe_2)(\mu\text{-}Cl)]_2 + 2\,LiCl + 2\,SMe_2$$

Methyllithium (0.4% LiCl; 1.71 mL, 1.69 mmol) is added to a cooled (– 78°C) and stirred suspension of *trans*-$[PdCl_2(SMe_2)_2]$ (0.51 g, 1.68 mmol) in anhydrous diethyl ether (100 mL) under a nitrogen atmosphere in a three-necked, 250-mL, round-bottomed flask fitted with a nitrogen inlet and a septum. The suspension is stirred for 1 h at – 78°C, giving a clear colorless solution with some unreacted *trans*-$[PdCl_2(SMe_2)_2]$. Gradual warming of the mixture to – 15°C gives an orange solution with only traces of *trans*-$[PdCl_2(SMe_2)_2]$ evident. Hydrolysis with 0.2 mL of water and filtration at – 10°C, followed by evaporation of solvent in a vacuum at 0°C gives a black solid. The solid is extracted with dry acetone (5 × 5 mL) and filtered. Dry hexane (30 mL) is added and slow evaporation of solvents in vacuum at 0°C gives the product as a yellow, microcrystalline solid (0.16 g, 44%). $^1$H NMR in $CDCl_3$: $\delta$ 2.34 ($SMe_2$), 0.78 (PdMe).

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*Anal.* Calcd. for C, 16.5; H, 4.1. Found: C, 16.6; H, 3.7.

## E. DIMETHYLBIS(DIMETHYLSULFIDE)DI($\mu$-BROMO)-DIPALLADIUM(II)

$$trans\text{-}[PdBr_2(SMe_2)_2] + LiMe \rightarrow 1/2\,[PdMe(SMe_2)(\mu\text{-}Br)]_2 + 2\,LiBr + 2\,SMe_2$$

The procedure outlined above is followed, using *trans*-$[PdBr_2(SMe_2)_2]$ (0.50 g, 1.28 mmol) and LiMe (1.22 mL, 1.28 mmol). The yield of the orange-tan product is 0.23 g (68%). $^1$H NMR in $CDCl_3$: $\delta$ 2.43 ($SMe_2$), 0.87 (PdMe).

*Anal.* Calcd. for C, 13.7; H, 3.4. Found: C, 13.8; H, 3.4.

## F. DIMETHYLBIS(DIMETHYLSULFIDE)DI($\mu$-IODO)-DIPALLADIUM(II)

$$trans\text{-}[PdCl_2(SMe_2)_2] + 2\,LiMe + MeI \rightarrow 1/2\,[PdMe(SMe_2)(\mu\text{-}I)]_2 + 2\,LiCl + SMe_2$$

The reaction given above is assumed to occur via the formation of dimethylpalladium(II) species which react with iodomethane to give ethane and the monomethylpalladium(II) product. The general procedure outlined for the synthesis of $[PdMe_2(\text{pyridazine})]_n$ is employed, using the same quantities of palladium(II) reagent, methyllithium, and diethyl ether solvent, but iodomethane (1.0 mL, 16.5 mmol) in diethyl ether (10 mL) is added in place of pyridazine. The resulting mixture is stirred at $-40^\circ$C (dry ice/acetone bath) for 1 h, followed by gradual warming to $-15^\circ$C to give a clear, yellow solution. Hydrolysis with 2 mL of water at $-15^\circ$C, filtration, and evaporation of diethyl ether solvent in a vacuum at 0°C gives the product as a yellow-green solid (0.41 g, 80%). Recrystallization is not necessary, although acetone/hexane is a suitable solvent system. The yield is 0.23 g (68%). $^1$H NMR in $CDCl_3$: $\delta$ 2.39 ($SMe_2$), 0.93 (PdMe).

*Anal.* Calcd. for C, 11.6; H, 2.9. Found: C, 11.9; H, 2.8.

### *Properties of the Complexes $[PdMe(SMe_2)(\mu\text{-}X)]_2$*

The complexes may be stored at $-20^\circ$C for many weeks without any visible sign of decomposition or deterioration of synthetic utility. They are soluble in dichloromethane and chloroform, and partially soluble in acetone. Exchange

reactions have been successfully accomplished in these solvents and in diethyl ether and benzene.

## G. DIMETHYL (*N,N,N′,N′*-TETRAMETHYLETHYLENEDIAMINE)-PALLADIUM(II)

$$1/n[PdCl_2]_n + tmeda \rightarrow PdCl_2(tmeda)$$

$$PdCl_2(tmeda) + 2MeLi \rightarrow PdMe_2(tmeda) + 2LiCl$$

In a round-bottomed flask containing 200 mL of acetonitrile, 6.00 g (33.8 mmol) of palladium(II) chloride* is dissolved at reflux. The solution is cooled to ambient temperature and tetramethylenediamine, tmeda (6 mL, 40 mmol), is added. The yellow precipitate formed is collected by filtration, washed with diethyl ether (3 × 25 mL), and dried in vacuo. Yield: 9.61 g (97%). A suspension of $PdCl_2$(tmeda) (3.00 g, 10.2 mmol) in diethyl ether (50 mL) is cooled to $-40°C$ under a nitrogen atmosphere in a 100-mL Schlenk tube. Methyllithium (19 mL, 1.6 M in diethyl ether) is added and the mixture is allowed to warm slowly to 0°C after which stirring is continued for 1 h at this temperature. Water (20 mL) is added, upon which the brown suspension becomes black. The water layer is frozen (using liquid nitrogen), allowing decantation of the clear ether layer; conventional separating funnel techniques are also satisfactory. The water layer is extracted with diethyl ether (3 × 50 mL), the combined ether layers are evaporated to dryness, and the residue is dissolved in benzene (30 mL). The solution is filtered through Celite and the filter is rinsed with benzene (2 × 10 mL). Evaporation of the filtrate gives a white, crystalline solid, which was suspended in pentane (50 mL), collected on a sintered-glass filter, and dried in vacuo. Yield: 2.11 g (81%) of pure $PdMe_2$(tmeda).

If required, the product may be recrystallized by dissolution in diethyl ether (40 mL) and acetone (7 mL) with subsequent filtration of the solution. Addition of pentane (10 mL) and storage overnight at $-20°C$ gives colorless crystals (1.10 g, 43%). $^1$H NMR in $CD_3COCD_3$: $\delta$ 2.57, (S, $CH_2$), 2.40 (s, $NMe_2$), $-0.34$ (s, PdMe).

*Anal.* Calcd. for C, 38.0; H, 8.8; N, 11.1. Found: C, 38.0; H, 8.6; N, 11.0.

*Properties*

The white solid may be kept at $-20°C$ for months without apparent decomposition. The complex is very soluble in acetone, benzene,

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dichloromethane, tetrahydrofuran, and chloroform and slightly soluble in diethyl ether. Ligand-exchange reactions are best performed in benzene or acetone. If not freshly prepared, solutions of $PdMe_2$(tmeda) should be filtered through Celite to remove traces of palladium metal.

## H. CHLORO(METHYL)(*N,N,N′,N′*-TETRAMETHYLETHYLENEDIAMINE)PALLADIUM(II)

$$PdMe_2(tmeda) + MeCOCl \rightarrow PdClMe(tmeda) + MeCOMe$$

Acetyl chloride (0.25 mL, 3.5 mmol) is added to solution of $PdMe_2$(tmeda) (0.75 g, 3.0 mmol) in benzene (50 mL) at $\sim 5°C$ in a 100-mL, round-bottomed flask. The solution is stirred at this temperature for 1 h, after which the solvent is evaporated. The residue is stirred with pentane (50 mL) and subsequently collected on a sintered-glass filter. The crude product is washed on the filter with pentane ($2 \times 10$ mL) and diethyl ether ($2 \times 10$ mL) and dried in vacuo, giving a slightly yellow power (0.73 g, 90%).

Although it is not necessary, the product may be recrystallized via dissolution in dichloromethane (12 mL), filtration and addition of diethyl ether (15 mL) to induce slow precipitation, collection by filtration, and washing with diethyl ether ($2 \times 10$ mL) (0.50 g, 62%). $^1$H NMR in $CDCl_3$: $\delta$ 2.80–2.45 (m, $CH_2$), 2.67 (s, $NMe_2$), 2.57 (s, $NMe_2$), 0.48 (s, PdMe).

*Anal.* Calcd. for C, 30.8; H, 7.0; N, 10.3. Found: C, 30.5; H, 7.0; N, 10.3. (N.B.: The acetyl chloride (and the acetyl bromide used in the next preparation) should be checked for acetic acid contamination as the presence of this will severely lower the yield.)

## I. BROMO(METHYL)(*N,N,N′,N*-TETRAMETHYLETHYLENEDIAMINE)PALLADIUM(II)

$$PdMe_2(tmeda) + MeCOBr \rightarrow PdBrMe(tmeda) + MeCOMe$$

This complex is prepared in a manner similar to the chloro complex and obtained as a slightly yellow power (0.91 g, 97%). The product may be recrystallized by stirring with dichloromethane (50 mL), filtration, and addition of hexane (50 mL) to induce slow precipitation. The suspension is concentrated to ca. 10 mL and the product collected by filtration and washed with diethyl ether ($2 \times 10$ mL) and dried in vacuo (0.78 g, 83%). $^1$H NMR in $CDCl_3$: $\delta$ 2.80–2.48 (m, $CH_2$), 2.65 (s, $NMe_2$), 2.59 (s, $NMe_2$), 0.50 (s, PdMe).

*Anal.* Calcd. for C, 26.5; H, 6.0; N, 8.8. Found: C, 26.4; H, 6.1; N, 8.7.

## J. IODO(METHYL)(*N,N,N′,N′*-TETRAMETHYLETHYLENEDIAMINE)PALLADIUM(II)

$$PdMe_2(tmeda) + MeI \rightarrow PdIMe(tmeda) + MeMe$$

Methyl iodide (0.2 mL, 3.2 mmol) is added to an ice-cold solution of $PdMe_2$(tmeda) (0.67 g, 2.7 mmol) in acetone (5 mL) in a 100-mL, round-bottomed flask. A yellow precipitate is immediately formed, accompanied by ethane evolution. The suspension is stirred at this temperature for 15 min, after which hexane (80 mL) is added. The bright yellow powder is collected by filtration, washed with hexane (2 × 10 mL), and dried in vacuo (0.91 g, 94%). The product may be recrystallized via dissolution in dichloromethane (3.5 mL), filtration, and slow addition of hexane (25 mL) to induce slow crystallization. The suspension is then concentrated to 5 mL and the product collected and washed with hexane (10 mL) (0.59 g, 79%). $^1$H NMR in $CDCl_3$: $\delta$2.80–2.45 (m, $CH_2$), 2.63 (s, $NMe_2$), 2.62 (s, $NMe_2$), 0.45 (s, PdMe).

*Anal.* Calcd. for C, 23.1; H, 5.2; N, 7.7. Found: C, 23.1; H, 5.1; N, 7.5.

## K. SYNTHESIS OF DIMETHYL{BIS(1,1′-DIPHENYLPHOSPHINO)FERROCENE}PALLADIUM(II)

$$1/n[PdMe_2(C_4H_4N_2)]_n + Fe(C_5H_4PPh_2)_2 \rightarrow PdMe_2(dppf) + C_4H_4N_2$$

Acetone (20 mL) in a 50-mL, round-bottomed flask is deaerated by nitrogen purge, bis(1,1′-diphenylphosphino)ferrocene (dppf)* (0.25 g, 0.45 mmol) is added and $[PdMe_2(pyridazine)]_n$ is added to the stirred suspension. The mixture is stirred at ambient temperature for 15 min and filtered, and the solvent is removed from the filtrate in a vacuum to give crude [$PdMe_2$(dppf)] as an orange solid in near quantitative yield. Recrystallization is achieved by dissolution in acetone/dichloromethane (15 mL/5 mL), filtration, addition of hexane (15 mL), and slow removal of solvent in a vacuum to ca. 10 mL to give the product as a yellow powder (0.26 g, 68%). $^1$H NMR in $CDCl_3$: $\delta$ 7.64–7.71 (m, 4H) and 7.31–7.45 (m, 6H) [$C_6H_5$], 4.22 and 4.08 ('t', 4H) [$C_5H_4$], 0.13 (d, 2H, $J_{H\text{-}P}$ 3 Hz) [$PdCH_3$]. $^{31}P\{^1H\}$ NMR in $CDCl_3$: $\delta$ 20.7. $^{13}$C NMR: 127.8–134.7 (m) [$C_6H_5$], 71.6 and 74.8 (s) [$C_5H_4$], 8.52 (dd, $J_{C\text{-}H}$ 15 Hz, $J_{C\text{-}P}$ 109 Hz) [$PdCH_3$].

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*Anal.* Calcd. for C, 62.6; H, 5.0. Found: C, 62.3; H, 5.1.

## L. SYNTHESIS OF OTHER COMPLEXES FROM $[PdMe_2(pyridazine)]_n$ OR $[PdMe(SMe_2)(\mu\text{-}X)]_2$

The following complexes may be obtained similarly to $PdMe_2(dppf)$, with yields given in parentheses: *cis*-$PdMe_2(PPh_3)_2$] (55%), [$PdMe_2(bipy)$] (82%), *trans*-[$PdXMe(PPh_3)_2$] [X = Cl (75%), Br (79%), I (82%), [PdXMe(bipy)] [X = Cl (73%), Br (75%), I (79%)], [PdXMe(dppf)] [X = Cl (71%), Br (72%), I (70%)].

## M. *CIS*-DIMETHYLBIS(TRIPHENYLPHOSPHINE)PALLADIUM(II)

$$PdMe_2(tmeda) + 2\ PPh_3 \rightarrow \textit{cis}\text{-}PdMe_2(PPh_3)_2 + tmeda$$

In a 25-mL, round-bottomed flask, $PPh_3$ (0.22 g, 0.84 mmol) is added to a solution of $PdMe_2(tmeda)$ (0.10 g, 0.40 mmol) in benzene (5 mL). A precipitate is formed in a short time. After stirring for 45 min the solvent is removed in vacuo. The product is washed with hexane (2 × 20 mL) and dried in vacuo. The solid is redissolved in a mixture of dichloromethane (14 mL) and acetone (6 mL). Hexane (15 mL) is added and the solution is concentrated in vacuo, giving a white solid. The solid is washed with hexane (2 × 30 mL) and dried in vacuo (0.22 g, 85%). $^1H$ NMR in $CDCl_3$: $\delta$ 7.0–7.4 (m, 15H) [$C_6H_5$], 0.22 (dd, 3H, $J_{H\text{-}P}$ 4 and 7 Hz) [PdMe]. $^{31}P\{^1H\}$ NMR in $CDCl_3$: $\delta$ 24.0.

## N. *TRANS*-CHLORO(METHYL)BIS(TRIPHENYLPHOSPHINE)-PALLADIUM(II)

$$PdClMe(tmeda) + 2\,PPh_3 \rightarrow \textit{trans}\text{-}PdClMe(PPh_3)_2 + tmeda$$

In a 25-mL, round-bottomed flask, $PPh_3$ (0.25 g, 0.95 mmol) is added to a solution of PdClMe(tmeda) (0.12 g, 0.44 mmol) in dichloromethane (10 mL). A precipitate is formed within a few minutes, and after stirring for 45 min the solvent is removed in a vacuum and the white product is washed with hexane (3 × 10 mL) and dried in vacuo (0.29 g, 97%). $^1H$ NMR in $CDCl_3$: $\delta$ 7.70 (m, 12H), 7.39 (m, 18H) [$C_6H_5$], −0.01 (t, 3H, $J_{H\text{-}P}$ 6 Hz) [PdMe]. $^{31}P\{^1H\}$ NMR in $CDCl_3$: $\delta$ 30.9.

## O. SYNTHESIS OF $PPh_3$ AND dppf COMPLEXES FROM PdXMe(tmeda)

Using methods K and L, the following complexes can be obtained, with yields in parentheses: $PdMe_2(bpy)$ (86%), $PdMe_2(dppf)$ (85%),

*trans*-[PdXMe($PPh_3$)$_2$] [X = Br (91%), I (92%)], and [PdXMe(dppf)] [X = Cl (70%), Br (87%), I (70%)]. The yields reported for the dppf complexes are following recrystallization from dichloromethane/hexane. Acetone was used as a solvent for the synthesis of bromo and iodo complexes.

## P. CHLORO(METHYL)(2,2′-BIPYRIDYL)PALLADIUM(II)

$$PdClMe(tmeda) + bpy \rightarrow PdClMe(bpy) + tmeda$$

In a 25-mL, round-bottomed flask, bpy (0.065 g, 0.42 mmol) is added to a solution of PdClMe(tmeda) (0.11 g, 0.40 mmol) in dichloromethane (10 mL). After stirring for 45 min hexane (2 mL) is added. The last step is repeated three times and during this period a yellow precipitate is formed. The solvent is evaporated in vacuo and the resulting solid washed with hexane (2 × 10 mL) and dried in vacuo. The product is a mixture of starting material and the desired complex. To ensure complete conversion, the entire procedure is repeated four times, after which the pure, pale yellow product can be obtained by repeated recrystallization from dichloromethane/hexane (0.08 g, 63%). $^1$H NMR in $CDCl_3$: $\delta$ 9.17 (d, 1H), 8.65 (d, 1H), 7.91–8.12 (m, 4H), 7.52 (m, 2H) [bpy], 1.00 (s, 3H) [PdMe].

*Anal.* Calcd. for C, 42.4; H, 3.5; N, 8.9. Found: C, 41.4; H, 3.5; N, 8.6.

The analogous complexes PdBrMe(bpy) and PdIMe(bpy) can be prepared in a similar way to give yields of 61 and 41%, respectively.

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# 29. 2,4-PENTANEDIONATOGOLD(I) COMPLEXES AND 2,4-PENTANEDIONATOTHALLIUM

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The 2,4-pentanedionato or acetylacetonato (acac) complexes are useful synthetic intermediates because they react with protic acids through the reaction (1):[1]

$$[M](acac) + BH \rightarrow [M]B + Hacac \qquad (1)$$

In addition, the byproduct acetylacetone is very easily separated from the other reaction product. We have shown the utility of $[Au(acac)PPh_3]$ and of $PPN[Au(acac)_2]$ [PPN = bis(triphenylphosphoranylidene)ammonium = $N(PPh_3)_2$] in the synthesis of a great variety of organometallic and coordination gold(I) complexes (see Scheme 1).[2] Laguna et al. have also found interesting applications for these complexes.[3]

The preparation of $[Au(acac)PPh_3]$ was first reported by Lewis et al.[4] by the reaction of $[AuCl(PPh_3)]$ with Tl(acac), but few experimental details were given. We report here a simpler method that improves the yield and uses less Tl(acac) than that reported later by Ingold et al.[5]

Although Tl(acac) is a very useful thallium compound and is commercially available (Strem) it is very easily obtained by reacting the cheaper $Tl_2CO_3$ and acetylacetone as described below. We also report the synthesis of $PPN[AuCl_2]$, which is used to prepare $PPN[Au(acac)_2]$.

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