

Reactions of Bis(β -diketonato)palladium(II) and -platinum(II) with Tertiary Phosphines^{††}

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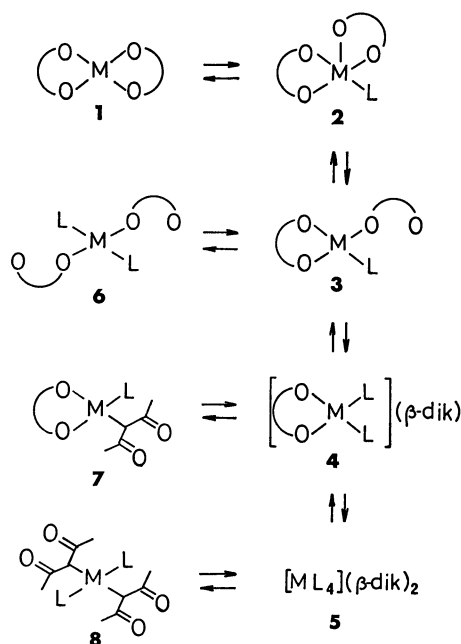
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Bis(β -diketonato)palladium(II) and -platinum(II) readily react with tertiary phosphines (L) to afford $[M(\beta\text{-dik})(\beta\text{-dik-O})L]$, $[M(\beta\text{-dik})L_2](\beta\text{-dik})$, $[ML_4](\beta\text{-dik})_2$, $[M(\beta\text{-dik-O})_2L_2]$, and $[M(\beta\text{-dik})(\beta\text{-dik-C})L]$ complexes, which were characterized mainly by infrared and ¹H and ¹³C NMR spectroscopy. Factors influencing the relative stability of each bonding mode of β -diketonate anions were investigated.

Since bis(2,4-pentanedionato)palladium(II) was found to react readily with Lewis bases such as triphenylphosphine, pyridine, and diethylamine to convert one of the chelating ligands into the central-carbon-bonded state,¹⁾ we have carried out comprehensive studies on the reactions of various bis(β -diketonato)palladium(II) and -platinum(II) complexes, $[M(\beta\text{-dik})_2]$, with a wide variety of nitrogen and phosphorus bases. In a previous paper^{2a)} the reactions of $[Pd(\beta\text{-dik})_2]$ with nitrogen bases were summarized in Scheme 1. Besides compounds **7** and **8** containing the carbon-bonded β -dik ligand, secondary and primary amines gave the cationic complexes **4** and **5**, respectively, which contain the β -dik anion as the counter ion in the outer sphere. In the platinum(II) case, compounds of the type **6** were also isolated as the linkage isomer of **4**.^{2,3)}

Since the kinetic study⁴⁾ revealed that compound **7** is produced *via* **4** and not directly from **1**, compound **4** seems to be formed *via* **3** which contains the oxygen-bonded β -dik as a unidentate ligand. However, no compounds of types **2** and **3** have been isolated in the reactions between $[M(\beta\text{-dik})_2]$ and nitrogen bases. Then the reactions with phosphorus bases have been examined, which proceed in a similar manner to those with nitrogen bases following Scheme 1, giving **2** and **3** as well as **4**, **5**, **6**, and **7**.

Several five-coordinate complexes $[M(\text{hfac})_2L]$ were prepared by the reactions of $[M(\text{hfac})_2]$ (M=Pd and Pt) with $P(o\text{-tolyl})_3$, PCy_3 , and $PPh(o\text{-tolyl})_2$ as L. The square-pyramidal structure of these complexes was inferred by the ¹H, ¹³C, and ¹⁹F NMR studies, and confirmed by X-ray analysis in the case of $[Pd(\text{hfac})_2P(o\text{-tolyl})_3]$ and $[Pt(\text{hfac})_2PCy_3]$.⁵⁾ Ito *et al.* also examined the reactions between $[Pt(\text{acac})_2]$ and phosphorus bases to obtain $[Pt(\text{acac-O})_2(PEt_3)_2]$ ⁶⁾ as well as $[Pt(\text{acac})(\text{acac-C}^3)L]$ (L= PPh_3 and PCy_3),⁷⁾ which were characterized by the NMR spectroscopy. The present paper reports the other new compounds obtained by the reactions of $[M(\beta\text{-dik})_2]$ (M=Pd and



Scheme 1.

Pt; β -dik=mainly acac, tfac, and hfac) as well as mixed-ligand chelates $[M(\text{acac})(\text{tfac})]$ and $[M(\text{acac})(\text{hfac})]$ with several kinds of tertiary phosphines.

Experimental

Preparation of Complexes. The starting bis(β -diketonato)palladium(II) and -platinum(II) complexes were prepared by the methods reported recently.⁸⁾ Most of tertiary phosphines were purchased and used without further purification, but less stable triethylphosphine was distilled under reduced pressure before use and tri-*o*-tolylphosphine was purified by recrystallization from ethanol.

1,1,1-Trifluoro-2,4-pentanedionato(1,1,1-trifluoro-2,4-pentanedionato-O)(tri-*o*-tolylphosphine)palladium(II), $[Pd(\text{tfac})(\text{tfac-O})\{P(o\text{-tolyl})_3\}]$ (3a**):** Hexane (10 cm³) was added to a red solution of $[Pd(\text{tfac})_2]$ (886 mg, 2.15 mmol) and $P(o\text{-tolyl})_3$ (663 mg, 2.18 mmol) in hot benzene (15 cm³) and the mixture was left to stand overnight at room temperature. Orange plates deposited were filtered, washed with diethyl ether (10 cm³) and air-dried. The yield was 1.12 g (73%).

$[Pd(\text{tfac})(\text{tfac-O})(PCy_3)]$ (3c**):** $[Pd(\text{tfac})_2]$ (151 mg, 0.366 mmol) and tricyclohexylphosphine (PCy_3) (110 mg, 0.392 mmol) were dissolved in dichloromethane (2 cm³) to result in a red solution. The solvent was allowed to evaporate spontaneously at room temperature to leave orange needles, which were recrystallized from hexane. The yield was 60 mg (24%).

^{††} In this paper the chelated, single oxygen bonded, and central carbon bonded anions of β -diketones such as 2,4-pentanedione (acacH), 1,1,1-trifluoro-2,4-pentanedione (tfacH), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), 1-phenyl-1,3-butanedione (bzacH), and 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (ttaH) are represented by β -dik, β -dik-O, and β -dik-C, respectively, and β -dik in the outer sphere shows a counter ion. Other abbreviations: PCy_3 , tricyclohexylphosphine; dpe, *cis*-1,2-bis(diphenylphosphino)ethylene; dppe, 1,2-bis(diphenylphosphino)ethane.

$[\text{Pd}(\text{acac})(\text{tfac-O})\{\text{P}(\text{o-tolyl})_3\}]$ (**3d**): Hexane (2 cm³) was added to a red solution of $[\text{Pd}(\text{acac})(\text{tfac})]$ (108 mg, 0.301 mmol) and $\text{P}(\text{o-tolyl})_3$ (94 mg, 0.31 mmol) in benzene (1.5 cm³), and the mixture was left to stand at ambient temperature to deposit orange yellow columns. The product was filtered, washed with petroleum ether (bp < 50 °C), and air-dried. The yield was 83 mg (42%).

$[\text{Pt}(\text{acac})(\text{acac-O})\{\text{P}(\text{o-tolyl})_3\}]$ (**3e**): A toluene solution (15 cm³) containing $[\text{Pt}(\text{acac})_2]$ (327 mg, 0.831 mmol) and $\text{P}(\text{o-tolyl})_3$ (1.024 mg, 3.36 mmol) was refluxed for 5.5 h. Hexane (20 cm³) was added to the solution and the mixture was left to attain room temperature. Yellow needles formed were filtered, washed with hexane and dried *in vacuo*. The yield was 393 mg (68%).

$[\text{Pt}(\text{tfac})(\text{tfac-O})\{\text{P}(\text{o-tolyl})_3\}]$ (**3f**): A solution of *cis*- $[\text{Pt}(\text{tfac})_2]$ (300 mg, 0.599 mmol) and $\text{P}(\text{o-tolyl})_3$ (203 mg, 0.667 mmol) in toluene (30 cm³) was heated under reflux for 3 h. The solvent was then distilled away under reduced pressure to leave a yellow powder, which was washed with diethyl ether. The product was dissolved in dichloromethane and recrystallized by addition of hexane to afford yellow needles (271 mg) in a 56% yield. A similar reaction of *trans*- $[\text{Pt}(\text{tfac})_2]$ also gave **3f** in a 48% yield.

$[\text{Pt}(\text{acac})(\text{tfac-O})\{\text{P}(\text{o-tolyl})_3\}]$ (**3h**): The reaction of $[\text{Pt}(\text{acac})(\text{tfac})]$ with three times molar amount of $\text{P}(\text{o-tolyl})_3$ and work up in a similar manner as above gave tiny white needles of **3h** in a 46% yield.

$[\text{Pt}(\text{acac})(\text{tfac-O})(\text{PPh}_3)]$ (**3i**): $[\text{Pt}(\text{acac})(\text{tfac})]$ (133 mg, 0.297 mmol) and triphenylphosphine (79 mg, 0.30 mmol) were dissolved in dichloromethane (1 cm³) and the solvent was allowed to evaporate spontaneously at room temperature to leave yellow needles, which were gathered, washed with hexane, and dried *in vacuo*. The yield was 125 mg (59%).

$[\text{Pt}(\text{acac})(\text{tfac-O})(\text{PEt}_3)]$ (**3j**): A dichloromethane solution (2 cm³) of triethylphosphine (25 mg, 0.21 mmol) was added dropwise to a solution of $[\text{Pt}(\text{acac})(\text{tfac})]$ (73 mg, 0.163 mmol) in the same solvent with stirring. The solvent was then allowed to evaporate spontaneously at room temperature to deposit colorless cubes. Recrystallization from dichloromethane–hexane gave white plates (11 mg) in a 12% yield.

Bis(tricyclohexylphosphine) (1,1,1-trifluoro-2,4-pentanedionato)-palladium(II), 1,1,1-Trifluoro-2,4-pentanedionate, $[\text{Pd}(\text{tfac})(\text{PCy}_3)_2](\text{tfac})$ (**4a**): $[\text{Pd}(\text{tfac})_2]$ (210 mg, 0.509 mmol) and PCy_3 (290 mg, 1.03 mmol) were dissolved in dichloromethane to afford an orange yellow solution. The solvent was allowed to evaporate spontaneously at room temperature to leave viscous red-orange oil, to which was added hexane (1 cm³) to deposit a yellow precipitate. Recrystallization from dichloromethane–hexane gave a yellow crystalline solid (116 mg) in a 33% yield.

$[\text{Pt}(\text{acac})(\text{PPh}_3)_2](\text{tfac})$ (**4d**): A solution of $[\text{Pt}(\text{acac})(\text{tfac})]$ (145 mg, 0.324 mmol) and PPh_3 (176 mg, 0.671 mmol) in diethyl ether was kept in a refrigerator for two days to precipitate white plates, which were filtered and dried *in vacuo*. The yield was 232 mg (74%).

Bis(cis-1,2-bis(diphenylphosphino)ethylene)palladium(II), 1,1,1-Trifluoro-2,4-pentanedionate, $[\text{Pd}(\text{dpe})_2](\text{tfac})_2$ (**5a**): To a suspension of $[\text{Pd}(\text{tfac})_2]$ (206 mg, 0.500 mmol) in dichloromethane (4 cm³) was added dpe (396 mg, 1.00 mmol) to result in a clear yellow solution, which on standing for several minutes began to deposit pale yellow plates. After being left overnight, the precipitate was filtered, washed with dichloromethane, and dried *in vacuo*. The yield was 536 mg (89%).

$[\text{Pd}(\text{PMe}_2\text{Ph})_4](\text{hfac})_2$ (**5b**): To a solution of $[\text{Pd}(\text{hfac})_2]$

(520 mg, 0.996 mmol) in diethyl ether (4 cm³) was added a solution of about four times molar amount of dimethylphenylphosphine (PMe_2Ph) (0.7 cm³) in the same solvent. Color of the solution changed immediately from red to orange yellow and yellow needles precipitated, which were filtered and washed five times with diethyl ether. Addition of hexane to a mixture of the filtrate and washings gave another crop of the product. The total yield of yellow crystals was 880 mg (82%).

$[\text{Pd}(\text{dpe})_2](\text{hfac})_2$ (**5c**): When dpe (159 mg, 0.401 mmol) was added to a solution of $[\text{Pd}(\text{hfac})_2]$ (104 mg, 0.199 mmol) in dichloromethane (1 cm³), the red color of the solution became light, precipitating white plates, which were filtered, washed with small portions of dichloromethane and diethyl ether, and dried *in vacuo*. The yield was 243 mg (92%).

$[\text{Pt}(\text{PMe}_2\text{Ph})_4](\text{tfac})_2$ (**5d**): On addition of a solution of PMe_2Ph (100 mg, 0.725 mmol) in diethyl ether (1 cm³) to a solution of *cis*- $[\text{Pt}(\text{tfac})_2]$ (106 mg, 0.212 mmol) in the same solvent, a creamy precipitate appeared immediately. After being washed three times with diethyl ether, the crude product (174 mg) was dissolved in hot dichloromethane (4 cm³). A small amount of petroleum ether was added to the solution to deposit a white crystalline solid, which was filtered and washed with acetone. The yield was 82 mg (37%).

$[\text{Pt}(\text{dppe})_2](\text{tfac})_2$ (**5e**): A white precipitate appeared immediately after addition of a solution of 1,2-bis(diphenylphosphino)ethane (dppe) (130 mg, 0.327 mmol) in dichloromethane (3 cm³) to a solution of $[\text{Pt}(\text{tfac})_2]$ (80 mg, 0.16 mmol) in the same solvent (3 cm³). Recrystallization from dichloromethane–hexane gave colorless columns (96 mg) in a 46% yield.

$[\text{Pt}(\text{dppe})_2](\text{hfac})_2$ (**5h**) and $[\text{Pt}(\text{dppe})_2](\text{acac})(\text{tfac})$ (**5j**): Similar reactions of $[\text{Pt}(\text{hfac})_2]$ and $[\text{Pt}(\text{acac})(\text{tfac})]$ with dppe in dichloromethane gave colorless plates of **5h** and pale yellow crystals of **5j** in 65 and 64% yields, respectively.

$[\text{Pd}(\text{dpe})_2](\text{tfac})_2 \cdot 1/4\text{CH}_2\text{Cl}_2$ (**5f**): To a solution of *cis*- $[\text{Pt}(\text{tfac})_2]$ (170 mg, 0.339 mmol) in dichloromethane (5 cm³) was added dpe (278 mg, 0.702 mmol). After being left overnight, white plates produced were filtered, washed with dichloromethane, and dried *in vacuo*. The yield was 415 mg (93%).

$[\text{Pt}(\text{dpe})_2](\text{hfac})_2$ (**5i**): White plates of **5i** were similarly prepared by the reaction between $[\text{Pt}(\text{hfac})_2]$ and dpe in dichloromethane. The yield was 96%.

$[\text{Pt}(\text{PMe}_2\text{Ph})_4](\text{hfac})_2$ (**5g**): White columns of **5g** (109 mg) were obtained in a 38% yield by the reaction of $[\text{Pt}(\text{hfac})_2]$ (150 mg, 0.246 mmol) with PMe_2Ph (115 mg, 0.833 mmol) in diethyl ether (3 cm³).

Bis(1,1,1-trifluoro-2,4-pentanedionato-O)bis(triethylphosphine)-platinum(II), $[\text{Pt}(\text{tfac-O})_2(\text{PEt}_3)_2]$ (**6a**): To a solution of *cis*- $[\text{Pt}(\text{tfac})_2]$ (72 mg, 0.14 mmol) in dichloromethane (0.5 cm³) was added PEt_3 (35 mg, 0.30 mmol) followed by a small amount of petroleum ether and the mixture was left overnight to allow spontaneous evaporation of the solvents. Colorless plates left were gathered, washed with a mixture of diethyl ether and ethanol (1:1 by volume) followed by neat ether, and air-dried. The yield was 67 mg (63%). *trans*- $[\text{Pt}(\text{tfac})_2]$ also gave the same product in ca. 50% yield.

$[\text{Pt}(\text{tfac-O})_2(\text{PCy}_3)_2]$ (**6b**): The reaction of $[\text{Pt}(\text{tfac})_2]$ with PCy_3 in a similar manner as above afforded yellow plates of **6b** in an 87% yield. Recrystallization from dichloromethane–hexane gave rise to colorless transparent plates, which became opaque on drying *in vacuo*. The final yield was 112 mg (50%).

$[\text{Pt}(\text{acac-O})(\text{tfac-O})(\text{PEt}_3)_2]$ (**6c**): Addition of a dichloromethane solution (0.5 cm³) of PEt_3 (57 mg, 0.48 mmol)

to a solution of $[\text{Pt}(\text{acac})(\text{tfac})]$ (81 mg, 0.18 mmol) in the same solvent (1 cm³) changed the solution colorless. Hexane (2 cm³) was added to the solution and the mixture was left standing overnight at room temperature. The mixed solvent was then evaporated spontaneously to deposit colorless plates, which were washed repeatedly with ethanol until odor of the phosphine was lost and dried *in vacuo*. The yield was 89 mg (79%).

2,4-Pentanedionato(2,4-pentanedionato-C³)(triethylphosphine)palladium(II), $[\text{Pd}(\text{acac})(\text{acac-C}^3)(\text{PEt}_3)]$ (**7a**): Triethylphosphine (43 mg, 0.36 mmol) was added dropwise to a solution of $[\text{Pd}(\text{acac})_2]$ (101 mg, 0.331 mmol) in chloroform (0.4 cm³) with stirring. After addition of petroleum ether (0.5 cm³) to the solution, the solvent mixture was vaporized spontaneously at ambient temperature to deposit yellow plates on the wall of vessel, which were filtered and washed with a mixture of ethanol and hexane (1:5 by volume). The yield was 31 mg (22%).

$[\text{Pd}(\text{acac})(\text{acac-C}^3)(\text{PMePh}_2)]$ (**7c**): To a suspension of $[\text{Pd}(\text{acac})_2]$ (76 mg, 0.25 mmol) in benzene (2 cm³) was added PMePh_2 (52 mg, 0.26 mmol) to result in a red solution. After addition of petroleum ether (2 cm³) to the solution, the solvent mixture was allowed to evaporate spontaneously at room temperature to leave yellow plates on the wall, which were gathered and washed with diethyl ether. The crude product (74 mg, 59% yield) was dissolved in dichloromethane and recrystallized as yellow cubes on addition of petroleum ether. The final yield was 40 mg (32%).

1-Phenyl-1,3-butanedionato(1-phenyl-1,3-butanedionato-C²)(triphenylphosphine)palladium(II), $[\text{Pd}(\text{bzac})(\text{bzac-C}^2)(\text{PPh}_3)]$ (**7d**): A mixture of $[\text{Pd}(\text{bzac})_2]$ (100 mg, 0.233 mmol) and PPh_3 (61 mg, 0.23 mmol) in diethyl ether (2 cm³) was stirred for *ca.* 4 h at room temperature. A yellow precipitate formed was filtered and washed with diethyl ether. The yield was 57 mg (35%). Recrystallization was performed from dichloromethane-hexane.

1-(2-Thienyl)-4,4,4-trifluoro-1,3-butanedionato[1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionato-C²](triphenylphosphine)palladium(II), $[\text{Pd}(\text{tta})(\text{tta-C}^2)(\text{PPh}_3)]$ (**7e**): The reaction of $[\text{Pd}(\text{tta})_2]$ with equimolar PPh_3 in diethyl ether in a similar manner as above gave a yellow powder of **7e** in a 60% yield.

Measurements. Infrared spectra were obtained in Nujol mull with Hitachi EPI-S and 295 infrared spectrophotometers. NMR spectra were recorded on JEOL-C60HL and JNM-MH100 (in the case of ¹H), FX60Q (for ¹H and ¹³C), and FX90Q (for ¹⁹F and ³¹P) instruments. Molecular weight was determined in dichloromethane at 27 °C with a vapor pressure osmometer manufactured by Knauer, West Berlin, West Germany.

Results and Discussion

Tertiary phosphines react quite readily with $[\text{M}(\beta\text{-dik})_2]$ (**1**) at room temperature. Table 1 lists the new compounds prepared by these reactions in appropriate organic solvents. In contrast to the case of nitrogen-base complexes, compounds **3** containing a tertiary phosphine as L and an O-unidentate β -dik ligand are sufficiently stable to be isolated and characterized. The π bonding between the d⁸ metals and the phosphine ligands may strengthen not only the M-L bond but also the M-O(β -dik) bond by decreasing the electron density at the metal atom. Furthermore bulky phosphines are prone to prevent for-

mation of the type **4** complexes.

In Table 2 are shown the infrared bands observed in the 1500–1800-cm⁻¹ region for the representative complexes of each type. The frequencies of these bands assignable to the $\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{C})$ vibrations are helpful for diagnosing the bonding mode of β -dik anions. Ito *et al* pointed out that the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ bands at 1650 and 1160 cm⁻¹, respectively, are characteristic of the unidentate acac ligand in $[\text{Pt}(\text{acac-O})_2(\text{PEt}_3)_2]$.⁶⁾ Each of compounds **3** and **6** also shows a band in the 1640–1660-cm⁻¹ region ascribable to the $\nu(\text{C}=\text{O})$ vibration of the O-bonded β -dik ligand. In addition, **3e** exhibits a strong $\nu(\text{C}-\text{O})$ band at 1165 cm⁻¹. In the case of the tfac and hfac complexes, however, very strong $\nu(\text{C}-\text{F})$ bands appear in the 1100–1200-cm⁻¹ region, making the absorption due to the $\nu(\text{C}-\text{O})$ vibration indiscernible.

Compared with **6**, compounds **3** show a few additional IR bands in the 1500–1625-cm⁻¹ region caused by the chelated β -dik ligand. The tfac and hfac anions involved in the outer sphere of compounds **4** and **5** exhibit a single band in the 1604–1612-cm⁻¹ and 1676–1680-cm⁻¹ regions, respectively. The latter frequency coincides with that (1670–1680 cm⁻¹) recorded for the corresponding hfac compounds **4** and **5** containing nitrogen bases as L.²⁾ On the other hand, the former frequency for the tfac anions in **4** and **5** is *ca.* 30 cm⁻¹ lower than that (1630–1640 cm⁻¹) observed for the corresponding nitrogen-base complexes.²⁾ The cause of this discrepancy is not rationalized at present. Compounds **7** show one or two bands in the 1650–1683-cm⁻¹ region assignable to the $\nu(\text{C}=\text{O})$ vibration of the C-bonded β -dik ligands.

¹H NMR Spectra. The ¹H NMR data for complexes **5** are listed in Table 3. A single set of the methyl and methine signals was observed for each complex, indicating that the two β -dik anions are environmentally equivalent. Much higher solubilities of **5** in methanol than in less polar solvents and absence of the Pt-H coupling in the proton signals from the β -dik anions in compounds **5d–5j** accord with the proposed salt-like structure. On the other hand, the methyl-proton signals from PMe_2Ph in **5d** and **5g** show coupling to platinum certifying that the phosphine is coordinated to the metal. The methine proton of the hfac anion in $[\text{Pd}(\text{PMe}_2\text{Ph})_4](\text{hfac})_2$ (**5b**) resonates at higher field (5.67 and 5.57 ppm in CDCl_3 and CD_3OD , respectively) than that in $[\text{Pd}(\text{hfac})_2]$ (6.42 and 6.50 ppm in respective solvents) because of the higher charge density on the noncoordinating anion. The methine signal from **5b** in C_6D_6 is shifted downfield by *ca.* 0.7 ppm, while the methyl signal from PMe_2Ph is shifted upfield by *ca.* 0.4 ppm as compared with the corresponding signals in CDCl_3 . Similar phenomena were noted previously for analogous complexes containing nitrogen bases and attributed to the stereospecific interaction between the square planar complex and benzene molecules.²⁾

In CD_3OD solution, the methine-proton signal from the tfac anion in **5** diminishes and instead a broad OH-proton signal becomes larger with time, attaining equilibrium in 2–3 h. Such a kind of H-D exchange is also observed in solutions of potassium β -diketonates

TABLE 1. ANALYTICAL DATA OF THE NEWLY PREPARED COMPLEXES,^{a)} $[\text{M}(\beta\text{-dik})(\beta\text{-dik-}O)\text{L}]$ (**3**), $[\text{M}(\beta\text{-dik})\text{L}_2](\beta\text{-dik})$ (**4**), $[\text{ML}_4](\beta\text{-dik})_2$ (**5**), $[\text{Pt}(\beta\text{-dik-}O)_2\text{L}_2]$ (**6**), AND $[\text{Pd}(\beta\text{-dik})(\beta\text{-dik-}C)\text{L}]$ (**7**)

Compd	M	$\beta\text{-dik}$	L	Dec temp °C	Found(Calcd)(%)	
					C	H
3a	Pd	tfac	P(<i>o</i> -tolyl) ₃	164—166	51.72(51.93)	4.03(4.08)
3c	Pd	tfac	PCy ₃	132—134	48.77(48.53)	6.02(5.96)
3d^{b)}	Pd	$\begin{cases} \text{acac} \\ \text{tfac} \end{cases}$	P(<i>o</i> -tolyl) ₃	160—165	56.11(56.16)	4.81(4.87)
3e	Pt	acac	P(<i>o</i> -tolyl) ₃	190—192	53.02(53.37)	4.98(5.06)
3f	Pt	tfac	P(<i>o</i> -tolyl) ₃	208—209	45.95(46.22)	3.57(3.63)
3h^{b)}	Pt	$\begin{cases} \text{acac} \\ \text{tfac} \end{cases}$	P(<i>o</i> -tolyl) ₃	220—226	49.43(49.53)	4.28(4.29)
3i^{b)}	Pt	$\begin{cases} \text{acac} \\ \text{tfac} \end{cases}$	PPh ₃	137—145	47.64(47.39)	3.68(3.69)
3j^{b)}	Pt	$\begin{cases} \text{acac} \\ \text{tfac} \end{cases}$	PEt ₃	135—138	34.02(33.98)	4.65(4.64)
4a	Pd	tfac	PCy ₃	122—124	55.61(56.76)	7.67(7.66)
4d^{b)}	Pt	$\begin{cases} \text{acac} \\ \text{tfac} \end{cases}$	PPh ₃	131—134	56.79(56.85)	4.27(4.25)
5a	Pd	tfac	$\frac{1}{2}\text{dpe}$	150—155	61.30(61.76)	4.34(4.35)
5b	Pd	hfac	PMe ₂ Ph	114—116	47.36(47.01)	4.38(4.32)
5c	Pd	hfac	$\frac{1}{2}\text{dpe}$	204—209	56.09(56.70)	3.61(3.53)
5d	Pt	tfac	PMe ₂ Ph	136—138	48.05(47.85)	4.91(4.97)
5e	Pt	tfac	$\frac{1}{2}\text{dppe}$	226—227	57.42(57.36)	4.40(4.35)
5f^{c)}	Pt	tfac	$\frac{1}{2}\text{dpe}$	202—203	56.68(56.84)	4.10(4.02)
5g	Pt	hfac	PMe ₂ Ph	168—170	43.48(43.42)	4.02(3.99)
5h	Pt	hfac	$\frac{1}{2}\text{dppe}$	280—284	53.11(52.96)	3.58(3.58)
5i	Pt	hfac	$\frac{1}{2}\text{dpe}$	≈ 238	52.66(53.11)	3.41(3.31)
5j	Pt	$\begin{cases} \text{acac} \\ \text{tfac} \end{cases}$	$\frac{1}{2}\text{dppe}$	208—213	58.75(59.85)	4.67(4.60)
6a	Pt	tfac	PEt ₃	146—147	35.93(35.82)	5.25(5.19)
6b	Pt	tfac	PCy ₃	196—199	52.32(52.02)	7.15(7.02)
6c	Pt	$\begin{cases} \text{acac} \\ \text{tfac} \end{cases}$	PEt ₃	145—146	39.03(38.65)	6.08(6.05)
7a	Pd	acac	PEt ₃	131—132	45.34(45.45)	6.97(6.91)
7c	Pd	acac	PMePh ₂	125—127	54.67(54.72)	5.42(5.39)
7d	Pd	bzac	PPh ₃	154—156	65.72(66.05)	4.85(4.81)
7e	Pd	tta	PPh ₃	115—125	49.81(50.35)	2.94(2.86)

a) The following compounds were not isolated, but characterized by IR and/or NMR spectroscopy in solution: $[\text{Pd}(\text{tfac})(\text{tfac-}O)(\text{PPh}_3)]$ (**3b**), $[\text{Pt}(\text{tfac})(\text{tfac-}O)(\text{PPh}_3)]$ (**3g**), $[\text{Pt}(\text{acac})(\text{hfac-}O)(\text{PPh}_3)]$ (**3k**), $[\text{Pd}(\text{tfac})(\text{PPh}_3)_2](\text{tfac})$ (**4b**), $[\text{Pt}(\text{tfac})(\text{PPh}_3)_2](\text{tfac})$ (**4c**), $[\text{Pt}(\text{acac})(\text{PPh}_3)_2](\text{hfac})$ (**4e**), $[\text{Pd}(\text{acac})(\text{acac-}C^3)(\text{PMe}_2\text{Ph})]$ (**7b**), and $[\text{Pd}(\text{tfac})(\text{tfac-}C^3)(\text{PPh}_3)]$ (**7f**). b) The acac ligand is chelated. c) Including $\frac{1}{4}\text{CH}_2\text{Cl}_2$.

in D₂O and the rate decreases in the sequence of basicity: acac > tfac > hfac. The same trend is noted in the present complexes **5**—CD₃OD systems, the hfac anion reacting very slowly except that in **5g** which attains the exchange equilibrium in 24 h. Of the two methine proton signals from $[\text{Pt}(\text{dppe})_2](\text{acac})(\text{tfac})$ (**5j**), the one at δ 5.56 attains the exchange equilibrium in 3 min but the signal at δ 5.30 diminishes very slowly. Thus the former signal is assigned to the acac anion and the latter to tfac. Previously the analogous compounds **4** and **5** containing amines as L were found to exchange the amine protons and the methine proton of $\beta\text{-dik}$ in the outer sphere with CDCl₃, the rate paralleling the basicity of $\beta\text{-dik}$.^{2,9)}

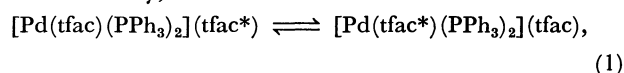
Compounds **4**, on the other hand, exhibit two sets of methyl and methine signals from tfac anions (Table 4). The signals assignable to acac in $[\text{Pt}(\text{acac})(\text{PPh}_3)_2](\text{tfac})$ (**4d**) are flanked by the ¹⁹⁵Pt satellites,

while those from tfac are not, indicating that acac was retained in and tfac was repelled from the coordination sphere in the reaction of $[\text{Pt}(\text{acac})(\text{tfac})]$ with PPh₃. When increasing amounts of PPh₃ was added to $[\text{Pt}(\text{acac})(\text{hfac})]$ in CDCl₃, signals assignable to $[\text{Pt}(\text{acac})(\text{hfac-}O)(\text{PPh}_3)]$ (**3k**) grew at first (*vide infra*). After the amount of PPh₃ exceeded the equimolar level, signals attributable to $[\text{Pt}(\text{acac})(\text{PPh}_3)_2](\text{hfac})$ (**4e**) appeared and increased gradually at the expense of the **3k** signals, which disappeared almost completely when three times molar PPh₃ was added. Thus the difference in the coordinating ability of $\beta\text{-dik}$ ligands in the mixed chelates is manifested by the reaction with PPh₃, the fluorinated $\beta\text{-dik}$ ligands being displaced in preference to acac.

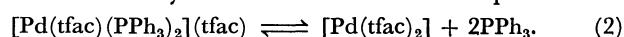
When twice molar PPh₃ reacted with *cis*- $[\text{Pt}(\text{tfac})_2]$ in CDCl₃, two sets of methyl and methine signals attributable to the tfac anions in $[\text{Pt}(\text{tfac})(\text{PPh}_3)_2]$ -

(tfac) (**4c**) were observed. Unfortunately, however, a spectrum distinct enough to allow the determination of exact coupling constants to ^{195}Pt could not be recorded, since the succeeding reactions gave rise to $[\text{Pt}(\text{tfac}(2-)-\text{C},\text{O})(\text{PPh}_3)_2]$ containing a C,O-chelated 1,1,1-trifluoro-2,4-pentanedionate dianion.¹⁰⁾ On the

contrary, the reaction mixture of $[\text{Pd}(\text{tfac})_2]$ and twice molar PPh_3 in CD_2Cl_2 at room temperature exhibited one set of broad methyl and methine signals, which became sharper with increasing temperature. At -45°C , on the other hand, two sets of sharp signals were observed and assigned to the tfac anions in the inner and outer spheres of $[\text{Pt}(\text{tfac})(\text{PPh}_3)_2]$ -(tfac) (**4b**), and the temperature change of spectrum was reversible. The proposed structure is also supported by the ^{13}C NMR spectroscopy (*vide infra*). It is not certain at the present stage whether the rapid interchange of the tfac anions at room temperature occurs directly,



or is effected by the forward and reverse processes of



The fact that $[\text{Pd}(\text{tfac})(\text{PCy}_3)_2](\text{tfac})$ (**4a**) shows no sign of the tfac exchange seems to suggest the associative nature of the ligand exchange, since the bulky PCy_3 ligands may prevent attack of tfac on palladium. Complex **4c** does not undergo the tfac exchange either, probably because of its substitution inertness as compared with the corresponding Pd(II) complex **4b**.

The methyl protons of the chelated β -dik ligands in complexes **4b**–**4e** resonate at δ 1.5–1.7. They are upfield shifted by 0.3–0.8 ppm compared with **4a** and complexes **4** containing nitrogen bases as L.²⁾ The phenyl rings of PPh_3 situated at the adjacent coordination sites seem to exert the anisotropic magnetic effect.^{1a)} Similar upfield shift of the methyl proton signals caused by the adjacent PPh_3 ligand is also noticed for complexes **3** and **7**.

TABLE 2. CHARACTERISTIC IR BANDS IN NUJOL (cm^{-1})

Compd	$\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{C})$
3a	1649 m, 1614 vs, 1588 m, 1515 vs
3d	1650 s, 1565 vs, 1510 vs
3e	1647 s, 1561 vs, 1525 vs
3f	1651 m, 1612 vs, 1600 sh, 1520 vs
3h	1646 m, 1564 vs, 1517 vs
3j	1641 s, 1575 vs, 1515 vs
4a	1610 vs, 1560 vs, 1535 sh
4b^{a)}	1610 vs, 1550 vs, br
4d	1604 m, 1588 s, 1555 vs, 1526 vs
5b	1678 vs, 1547 vs, 1529 vs
5d	1612 s, 1545 vs, br
5g	1676 vs, 1548 vs, 1528 vs
6a	1660 vs, 1513 vs, br
6b	1670 sh, 1660 vs, 1540 vs, br
6c	1646 s, 1510 vs, br
7a	1683 vs, 1650 vs, 1568 vs, br, 1515 vs
7d	1653 vs, 1558 vs, 1517 vs
7f^{b)}	1715 vs, 1665 s, 1615 vs, br, 1523 vs

a) In CDCl_3 . b) Orange red oil left after evaporation *in vacuo* of solvent from a solution of $[\text{Pd}(\text{tfac})(\text{tfac}-\text{C}^3)-(\text{PPh}_3)]$ (**7f**) of which formation by the reaction of $[\text{Pd}(\text{tfac})_2]$ with equimolar PPh_3 in CDCl_3 was confirmed by ^1H NMR spectroscopy.

TABLE 3. ^1H NMR DATA FOR COMPLEXES $[\text{ML}_4](\beta\text{-dik})_2$ (**5**) AND *trans*- $[\text{Pt}(\beta\text{-dik-O})_2\text{L}_2]$ (**6**)^{a)}

Compd	Solvent	$\beta\text{-dik}$		L		
		CH_3	CH	CH_3	CH_2	Ph
5a	CD_3OD	2.28	5.25 ^{b)}			7.4 br ^{e)}
5b	CDCl_3		5.67	1.53		7.5 br
	C_6D_6		6.35	1.14		7.0–7.7 m
	CD_3OD		5.57	1.48		7.7 br
5c	CD_3OD		5.55			7.4 br ^{e)}
5d	CD_3OD	2.11	5.23 ^{b)}	1.57 br{25}		7.7 br
5e	CD_3OD	2.27	5.22 ^{b)}		2.7 ₃ m, br	7.5 br
5f	CD_3OD	2.29	5.24 ^{b)}			7.4 br ^{e)}
5g	CD_3OD		5.58 ^{b)}	1.58 br{25.4}		7.7 br
5i	CD_3OD		5.56			7.4 br ^{e)}
5j	CD_3OD	2.05 br ^{b)}	5.56 ^{b)}		2.77 m, br	7.8 br
		2.32 ^{c)}	5.30 ^{b,c)}			
6a	CDCl_3	2.37{4.4}	6.41{12.7}	1.22 [8] (8) ^{d)}	1.66 m	
6b	CDCl_3	2.36{4.5}	6.58{11}		1.3 br, 1.9 br	
6c	CDCl_3	2.23{6}	6.31{14}	1.20 [8] (8) ^{d)}	1.53 m	
		2.06				
		2.35{3} ^{c)}	6.49{12} ^{c)}			

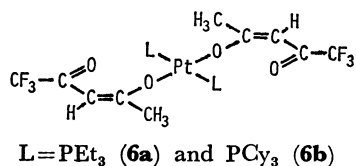
a) Chemical shifts in ppm from internal Me_4Si at 25°C . Figures in braces, brackets, and parentheses are $J(^{195}\text{Pt}-\text{H})$, $J(^{31}\text{P}-\text{H})$, and $^3J(\text{CH}_2-\text{CH}_3)$ in Hz, respectively. b) The intensity decreases with time due to the H-D exchange reaction with the solvent. c) Signals from the tfac anion. d) Quintet due to the virtual coupling between the ^{31}P atoms located at the mutually trans positions. e) This large signal masks that from the vinyl protons of dpe.

TABLE 4. ^1H NMR DATA FOR COMPLEXES $[\text{M}(\beta\text{-dik})\text{L}_2](\beta\text{-dik})$ (**4**)^{a)}

Compd	Solvent	$\beta\text{-dik}(\text{IS})$		$\beta\text{-dik}(\text{OS})$		$\text{L}^c)$ Ph or Cy
		CH_3	CH	CH_3	CH	
4a	CDCl_3	2.47	6.08	2.27	5.34	1.9 br, 1.4 br
4b ^{d)}	$\text{CD}_2\text{Cl}_2^e)$	2.01 br	5.47 br	2.01 br	5.47 br	7.36 br, 7.46 br
	$\text{CD}_2\text{Cl}_2^f)$	1.70	5.92	2.33	5.19	7.43 br
4c ^{d)}	CDCl_3	1.47{ ≈ 5 }	6.01	2.46	5.38	7.4 m, br
4d	CDCl_3	1.50{4}	5.51{6}	2.47	5.25	7.3 m, br
	CD_3OD	1.51{3}	5.65{6}	2.30 ^{b)}	5.23 ^{b)}	7.4 m, br
4e ^{d)}	CDCl_3	1.48{3}	5.54{5}		5.61	7.4 m, br, 7.7 m, br

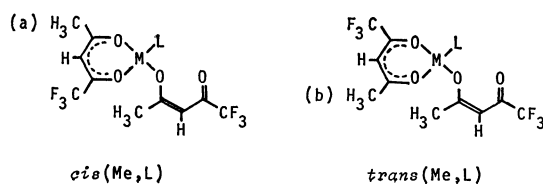
a), b) Same as footnotes for Table 3. IS and OS abbreviate the inner and outer spheres, respectively. c) L is PPh_3 except for **4a** which has PCy_3 as L. d) $[\text{M}(\text{tfac})(\text{PPh}_3)_2](\text{tfac})$, where $\text{M}=\text{Pd}$ (**4b**) and Pt (**4c**), were prepared in solution by the reactions of $[\text{M}(\text{tfac})_2]$ with twice molar PPh_3 , and $[\text{Pt}(\text{acac})(\text{PPh}_3)_2](\text{hfac})$ (**4e**) was formed by the reaction of $[\text{Pt}(\text{acac})(\text{hfac})]$ with excess PPh_3 . See text. e) The $\beta\text{-dik}$ anions in IS and OS are interchanging with each other rapidly at 25°C . f) At -45°C .

The ^1H NMR data for complexes **6** are included in Table 3. They are quite similar to those for *trans*- $[\text{Pt}(\text{acac}-\text{O})_2(\text{PEt}_3)_2]^6)$ and *trans*- $[\text{Pt}(\text{acac}-\text{O})_2(\text{pip})_2]^3)$ where pip represents piperidine. Each of **6a** and **6b** exhibits single tfac-methyl signal flanked by the ^{195}Pt satellites, indicating that the acetyl oxygen is preferentially bonded to the metal. The characteristic quintet resonance ($J=8\text{ Hz}$) of the methyl protons of PEt_3 in **6a** and **6c** suggests the *trans* arrangement of the PEt_3 ligands.¹¹⁾ Even when *cis*- $[\text{Pt}(\text{tfac})_2]$ reacted with the phosphine, the product was *trans*- $[\text{Pt}$ -



($\text{tfac}-\text{O}$) $_2\text{L}_2]$ exclusively. The *trans* configuration seems to be thermodynamically more stable and may have been realized by the geometrical isomerization catalyzed by the tertiary phosphine¹²⁾ contained in excess in the reaction mixture. The *cis*-*trans* isomerization may proceed by means of the intramolecular rearrangement of a five-coordinate intermediate. The dynamic behavior in solution of the five-coordinate complexes $[\text{M}(\text{hfac})_2\{\text{P}(o\text{-tolyl})_3\}]$ ($\text{M}=\text{Pd}$ and Pt) was elucidated by the ^{13}C and ^{19}F NMR spectroscopy and interpreted based on a proposed mechanism.⁵⁾

Complexes **3** are stable in solution. Molecular weights of **3a** and **3e** were determined in dichloromethane to be 716 and 659, which are near the calculated values, 717 and 698, respectively. The ^1H NMR data for **3** are listed in Table 5. Since the tfac anion is unsymmetric, the following two geometrical isomers are conceivable even though the unidentate tfac is bound to the metal preferentially *via* the more basic acetyl oxygen as was the case for com-



plexes **6**. Thus four tfac-methyl signals are observed for **3f** at 1.63, 1.92, 1.97, and 2.11 ppm with the area ratio of 1:1:4:4, disclosing coexistence of the two isomers in the 1:4 ratio. The signal at the highest field is readily assigned to $\text{CH}_3(\text{a})$ of the chelating tfac in the *cis*(Me, L) isomer and in turn the signal at δ 1.92 to CH_3 of the O-unidentate tfac in the same isomer. The remaining signals at δ 1.97 and 2.11 are attributed to the *trans*(Me, L) isomer, but discrimination of them is not straightforward. The higher-field signal (δ 1.97) near the above one at δ 1.92 is tentatively assigned to CH_3 of the O-unidentate tfac and the one at δ 2.11 to $\text{CH}_3(\text{b})$ of the chelating tfac. The assignment is supported by the fact that the methyl protons of the chelating tfac in the *trans*(Me, L) isomer of $[\text{Pd}(\text{tfac})(\text{tfac}-\text{C}^3)(\text{PPh}_3)]$ (**7f**) also resonate at 2.22 ppm. It is noteworthy that the $\text{CH}_3(\text{a})$ protons couple to ^{195}Pt ($^4J=4\text{ Hz}$) but $\text{CH}_3(\text{b})$ does not in accordance with the higher *trans* influence of the tertiary phosphine than that of the O-unidentate $\beta\text{-dik}$ which is shown by the following ^{31}P NMR data.

Figure 1 displays the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3f** in CDCl_3 . Two overlapping triplets are observed at 72.81 and 72.96 ppm upfield from external CFCl_3 ,

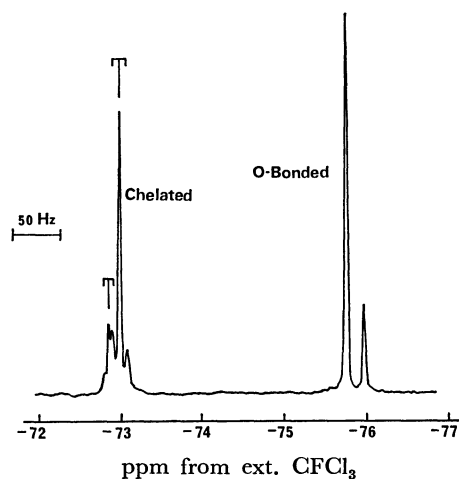


Fig. 1. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum at 84.31 MHz of $[\text{Pt}(\text{tfac})(\text{tfac}-\text{O})\{\text{P}(o\text{-tolyl})_3\}]$ (**3f**) in CDCl_3 .

TABLE 5. ^1H NMR DATA FOR COMPLEXES **3** AND **7** IN CDCl_3 ^{a)}

Compd	cis trans	Isomer	Chelated β -dik			Unidentate β -dik		L	
			CH_3 (a)	CH_3 (b)	CH	CH_3	CH	CH_3	Ph ^{b)}
3a	$\frac{1}{5}$	cis trans	1.74		c) 5.76	1.89 1.94	c) 5.84	2.29	7.87 dd[12](7), 1.9 br, 1.3 br
3b		cis ^{e)} trans		2.23	5.90	2.02	6.27		7.5 m, br
3c	$\frac{1}{5}$	cis trans	2.13		5.70 5.94	2.17 2.20	5.94 6.30		Cy: 1.9 br, 1.3 br
3d			1.56	2.05	5.44	1.93	5.91	2.33	7.88 dd[13](8), 7.2—7.6 m
3e			1.46{4}	1.98	5.43{6.5}	1.89, 1.82	5.72{7.5}	2.29	7.78 dd[13](7), 7.1—7.5 m
3f	$\frac{1}{4}$	cis trans	1.63{4}		c) 5.85{6.5}	1.92 1.97{ $\approx$ 4}	c) 5.94{7.5}	2.27	7.84 dd[13](7), 7.2—7.6 m
3g	$\approx \frac{1}{4}$	cis trans	1.72{4}		c) 5.92	c) 1.97	c) 6.33		7.4 m, br
3h			1.48{5}	1.95	5.43{7.5}	1.95	5.88	2.28	7.82 dd[15](7), 7.0—7.4 m
3i			1.64{5}	2.00	5.52{7}	2.00{ $\approx$ 3}	6.39{8}		7.2—7.8 m
3i^{d)}			1.45{5}	1.81	5.23{7.5}	2.05{4}	6.44{9}		7.1—7.7 m
3j			c)	c)	5.48	c)	6.47		Et: c)
3k			1.54{5}	1.90	5.42{9}		5.59		7.3—7.9 m
7a			1.84	1.94	5.09	2.20	3.53[4]	1.26(6)	CH_2 : 1.5—2.1 m
7b			1.92	1.99	5.37	2.06	3.55[5]	1.78[11]	7.2—7.8 m
7c			1.64	2.02	5.51	2.17	3.72[5]	2.11[11]	7.2—7.8 m
7d^{e)}	$\frac{1}{1}$	cis trans	1.55		5.94 5.98	2.60 2.58	4.38[5.4]		
7e^{f)}	$\frac{1}{1}$				6.20 6.23		4.41[5] 4.34[5]		Ph and thienyl: 7.2—7.8 m
7f	$\frac{1}{3}$	cis trans	1.65		5.75 5.76	2.43 2.41	3.91[4] 3.98[4]		7.3—7.8 m

a) Same as footnote(a) for Table 3. Cis and trans abbreviate *cis*(Me,L) and *trans*(Me,L), respectively. See text. b) dd: doublet of doublets. The coupling constants $^3J(\text{P-H})$ and $^3J(\text{C-H})$ are given in brackets and parentheses, respectively. c) Indiscernible because of overlapping with other signals. d) Determined in a mixture of CDCl_3 and C_6D_6 (2:1 by volume). e) Phenyl protons of the bzac and PPh_3 ligands resonate at 6.9—7.9 ppm. f) Two isomers coexist in approximately equal proportions but are indistinguishable.

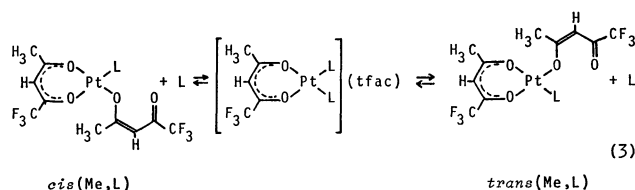
$^4J(\text{Pt-F})$ being *ca.* 10 and 16 Hz, respectively. On the basis of their relative intensities, the more intense higher-field signal is assigned to CF_3 of the chelating tfac in the *trans*(Me,L) isomer and the lower-field one to that in the *cis*(Me,L) isomer. Two sharp singlets observed at 75.74 and 75.97 ppm upfield from external CFCl_3 with the area ratio of 4:1 are assigned to the CF_3 groups of unidentate tfac in the *trans*(Me,L) and *cis*(Me,L) isomers, respectively. It should be noted that the dangling CF_3CO group has no bonding interaction with the platinum atom, exhibiting a sharp ^{19}F singlet. The five coordinate complex $[\text{Pt}(\text{hfac})_2\{\text{P}(o\text{-tolyl})_3\}]$ containing the phosphine ligand in the basal plane of a square pyramid structure⁵⁾ exhibits an analogous ^{19}F NMR spectrum, but the higher-field singlet is broad, indicating coupling to platinum.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3f** in CDCl_3 shows two signals at 4.5₁ and 5.2₅ ppm upfield from external H_3PO_4 flanked by the ^{195}Pt satellites with $^1J(\text{Pt-P}) = 4410$ and 4380 Hz, respectively. Based on the relative intensities, they are assigned to the *cis*(Me,L) and *trans*(Me,L) isomers, respectively. The minor

signal at 4.5₁ appears as a quartet with $^5J(\text{F-P}) = 1.1$ Hz, certifying that the CF_3 group occupies the *trans* position to the phosphine ligand in the *cis*(Me,L) isomer. The larger $^1J(\text{Pt-P})$ value for the *cis*(Me,L) isomer than that for *trans*(Me,L) suggests that the poorer donor-ability of the CF_3CO moiety than that of CH_3CO decreases the charge density at platinum, suppressing the π -character and increasing the σ -character of the *trans* Pt-P bond.

Complex **3f** was produced by the reaction of $\text{P}(o\text{-tolyl})_3$ with either of *cis*- and *trans*- $[\text{Pt}(\text{tfac})_2]$ and the ratio of *cis*(Me,L) and *trans*(Me,L) is almost constant. Geometrical isomerization catalyzed by the tertiary phosphine *via* a five-coordinate intermediate as mentioned above may have occurred to result in the equilibrium mixture of **3f**, since the bulkiness (cone angle 194°)¹³⁾ of $\text{P}(o\text{-tolyl})_3$ seems to make the consecutive substitution mechanism (Eq. 3) *via* a bis(phosphine) complex less probable.

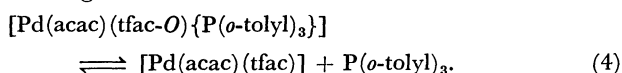
$[\text{Pt}(\text{acac})(\text{acac-O})\{\text{P}(o\text{-tolyl})_3\}]$ (**3e**) exhibits four acetyl-methyl signals, which were assigned by reference to **3f** and $[\text{Pt}(\text{acac})(\text{acac-C}^3)(\text{PPh}_3)]$.⁷⁾ Proton res-



onances from other complexes **3** were assigned in a similar way and listed in Table 5. It should be noted that the $\text{CH}_3(\text{a})$ protons in $[\text{Pd}(\text{tfac})(\text{tfac}-O)(\text{PCy}_3)]$ (**3c**) resonate at much lower field as 2.13 ppm than those in other complexes containing the triarylphosphine as L.

$[\text{Pt}(\text{acac})(\text{tfac}-O)\{\text{P}(o\text{-tolyl})_3\}]$ (**3h**) exhibits two acetyl-methyl signals at 1.48 and 1.95 ppm in the area ratio of 1:2. The peak at δ 1.48 is assigned to $\text{CH}_3(\text{a})$ of the chelated acac and the other to $\text{CH}_3(\text{b})$ of acac and CH_3 of the O-unidentate tfac which resonate at the same field accidentally. If tfac were chelated alternatively to Pt and acac served as the unidentate ligand, more peaks (at most six) should appear, since two geometrical isomers are possible and the unidentate acac should exhibit two separate methyl signals. The corresponding palladium(II) complex **3d** shows three signals at 1.56, 2.05, and 1.93 ppm, of which the former two are assigned to the chelated acac and the last one to the unidentate tfac in a similar manner as above.

Thus the chelated tfac has stronger tendency than acac to transform into the O-unidentate state. In fact $[\text{Pd}(\text{acac})_2]$ did not react with three times molar $\text{P}(o\text{-tolyl})_3$ even when kept in boiling toluene for 5 h, whereas $[\text{Pd}(\text{tfac})(\text{tfac}-O)\{\text{P}(o\text{-tolyl})_3\}]$ (**3a**) was formed in a good yield when equimolar amounts of $[\text{Pd}(\text{tfac})_2]$ and $\text{P}(o\text{-tolyl})_3$ were mixed in hot benzene and the mixture was kept overnight at room temperature. However, compound **3d** is not so stable in CDCl_3 , but about 30% of $\text{P}(o\text{-tolyl})_3$ is liberated according to



On addition of excess phosphine, the equilibrium is shifted to left and proton signals from $[\text{Pd}(\text{acac})(\text{tfac})]$ disappears. On the contrary, complex **3h** is quite stable in solution and shows no sign of dissociation. Thus the platinum(II) complexes of type **3** seem more stable than the corresponding palladium(II) complexes.

The proton signal pattern of $[\text{Pt}(\text{acac})(\text{tfac}-O)(\text{PPh}_3)]$ (**3i**) in CDCl_3 resembles quite well to that of **3h**. On addition of C_6D_6 to this solution, the overlapped methyl signal at 2.00 ppm was separated, giving rise to three equi-intensity methyl signals. It has been reported that as compared with the spectra in other solvents, C_6D_6 shifts the methyl and methine signals from the chelated $\beta\text{-dik}$ to the higher field and those from $\beta\text{-dik}$ in the outer sphere to the lower field.^{2,8b)} The δ 1.45, 1.81, and 5.23 signals observed in the mixed solvent lie in the higher field than the corresponding ones in CDCl_3 and are assigned to $\text{CH}_3(\text{a})$, $\text{CH}_3(\text{b})$, and CH of the chelated acac, respectively. The remaining peaks at δ 2.05 and 6.44 are then ascribed to CH_3 and CH of the unidentate

tfac, indicating that C_6D_6 shifts these resonances to the lower field in a similar way as it shifts the signals from $\beta\text{-dik}$ in the outer sphere. Thus the two CH signals for **3i** were distinguished, the higher-field one being assigned to the chelated $\beta\text{-dik}$ and the lower-field one to the O-unidentate $\beta\text{-dik}$. Similarly methine signals from each of compounds **3** were distinguished and listed in Table 5.

When PEt_3 was added in small portions to CDCl_3 solutions of $[\text{Pt}(\text{acac})_2]$ and $[\text{Pt}(\text{tfac})_2]$, proton signals attributable to $[\text{Pt}(\beta\text{-dik}-O)_2(\text{PEt}_3)_2]$ (**6**) appeared, but those assignable to the intermediate complexes **3** could not be observed. On the other hand, addition of PEt_3 to a solution of $[\text{Pt}(\text{acac})(\text{tfac})]$ in CDCl_3 gave rise to new signals at 5.48 and 6.47 ppm, which are assigned to methine protons of $[\text{Pt}(\text{acac})(\text{tfac}-O)(\text{PEt}_3)]$ (**3j**). Methyl resonances of **3j** were indiscernible because of overlapping with signals from **6c**, successor of **3j**. In a similar manner, addition of PPh_3 in limited amounts to a CDCl_3 solution of $[\text{Pt}(\text{acac})(\text{hfac})]$ produced proton signals due to $[\text{Pt}(\text{acac})(\text{hfac}-O)(\text{PPh}_3)]$ (**3k**) as recorded in Table 5. Compound **3j** was isolated, while **3k** was not. However, characterization of these compounds in solution suggests that compounds $[\text{Pt}(\text{acac})(\beta\text{-dik}-O)\text{L}]$ containing chelated acac and unidentate $\beta\text{-dik}$ other than acac are more stable than the corresponding compounds **3** containing one kind of $\beta\text{-dik}$.

As is noticed in Table 5, the *trans*(Me,L) isomers of compounds **3** containing tfac are invariably more stable than the *cis*(Me,L) isomers. The σ -donating ability of the CH_3CO moiety is higher than that of the CF_3CO moiety, strengthening the Pt-phosphine π -bonding. Although the σ -character of the Pt-P bond is decreased in this case as was evidenced by the lower $^1J(\text{Pt-P})$ value for *trans*(Me,L)-**3f** than that for the *cis* isomer, the overall stability of the *trans*(Me,L) isomer is higher, suggesting that the π -bonding of Pt-phosphine is more important than the σ -bonding in these complexes.

The ^1H NMR spectrum of the O-unidentate acac was first recorded for $\text{R}_3\text{Si}(\text{acac}-O)$ by Pinnavaia and his collaborators.¹⁴⁾ It is composed of two sets of signals assignable to two geometrical isomers. The *trans* isomer, in which the acetyl and R_3SiO groups occupy the *trans* positions around the C=C bond, exhibits a methine multiplet and two acac methyl doublets as the result of the spin-spin coupling between the methine proton and both methyl groups. On the other hand, the *cis* isomer shows a methine singlet and a methyl singlet due to a rapid fluxional motion at room temperature interchanging intramolecularly the coordinating oxygen atom of the unidentate acac ligand. The unidentate acac in **3e** and **6c** exhibits one methine and two methyl resonances showing no coupling to each other. Similarly the unidentate tfac in each of other compounds **3** and **6** gives only one set of mutually uncoupled methine and methyl signals for the *cis*(Me,L) or *trans*(Me,L) isomer. These results indicate that the unidentate acac and tfac ligands always have the stereochemically rigid *cis* structure as depicted above. The O-unidentate $\beta\text{-dik}$ originates from the O,O'-chelate and

cis configuration around the C=C bond was reserved during the reactions with phosphines under the mild conditions.

Table 5 includes the ^1H NMR data for complexes **7** inclusive of **7b** and **7f** which were not isolated. Proton signals from $[\text{Pd}(\text{acac})(\text{acac}-C^3)\text{L}]$ ($\text{L}=\text{PEt}_3$ (**7a**), PMe_2Ph (**7b**), and PMePh_2 (**7c**)) were assigned by reference to $[\text{Pd}(\text{acac})(\text{acac}-C^3)(\text{PPh}_3)]$.^{1a} There exist *cis*(Me,L) and *trans*(Me,L) isomers in the case of **7d**, **7e**, and **7f** containing unsymmetrical β -dik, and the signals were assigned by reference to the data for $[\text{Pt}(\text{etac})(\text{etac}-C^2)(\text{PPh}_3)]$,¹⁵ of which etac represents the 1-ethoxy-1,3-butanedionate anion. Since $[\text{Pd}(\text{tta})(\text{tta}-C^2)(\text{PPh}_3)]$ (**7e**) lacks the methyl group, the geometrical isomers are indistinguishable though two sets of methine signals indicate their coexistence. When an equimolar amount of PPh_3 was added to a solution of $[\text{Pd}(\text{tfac})_2]$ in CDCl_3 , proton signals ascribable to $[\text{Pd}(\text{tfac})(\text{tfac}-O)(\text{PPh}_3)]$ (**3b**) appeared first followed by those due to $[\text{Pd}(\text{tfac})(\text{tfac}-C^3)(\text{PPh}_3)]$ (**7f**), which is more stable and was the sole product after 1 h. $[\text{Pd}(\text{bzac})(\text{bzac}-C^2)(\text{PPh}_3)]$ (**7d**) is also stable in dichloromethane, giving a molecular-weight value of 640 near the calculated value (691).

¹³C NMR Spectra.

The ¹³C NMR data for com-

pounds **5** are listed in Table 6. None of the carbon signals from β -dik in **5** is flanked by ¹⁹⁵Pt satellites, indicating that the β -dik anions are not coordinated with the metal atom. The CH_3 and CF_3 carbon signals from β -dik in the outer sphere show downfield shift of 2–4 ppm, while the CH carbon upfield shift of 3–10 ppm as compared with the corresponding carbons in $[\text{M}(\beta\text{-dik})_2]$. The $^1J(\text{C}-\text{F})$ value for compounds **5** is more than 5 Hz larger and $^2J(\text{C}-\text{F})$ is about 4 Hz smaller than those for the corresponding carbons in the bis-chelates. Similar trend was also noted for complexes of the type **5** containing nitrogen bases as L^2) and for $[\text{K}(18\text{-Crown-6})](\beta\text{-dik})$.

Compound **4a** exhibits two sets of carbon signals from β -dik, which were easily assigned as is listed in Table 7 based on the above information. The CH_3 carbon of the chelated tfac appears as a doublet of doublets due to coupling to both ³¹P atoms, $^4J(\text{P}-\text{C})$ being 5 Hz to *trans* P and 2 Hz to *cis* P. The CF_3 carbon, on the other hand, couples only to *trans* P ($^4J=9$ Hz). The acetyl carbon, CH_3CO , also couples only to *trans* P and the $^3J(\text{P}-\text{C})$ is smaller (2.5 Hz) than that for CH_3 which is remote from P. Similar situation is observed for $[\text{Pt}(\beta\text{-dik})_2]$,⁸⁾ the $^3J(\text{Pt}-\text{C})$ values for CH_3 , CF_3 , and CH are about twice

TABLE 6. ¹³C NMR DATA FOR $[\text{ML}_4](\beta\text{-dik})_2$ (**5**) IN CD_3OD^a

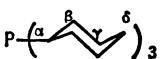
Compd	CH ₃	CF ₃	CH	CH ₃ CO	CF ₃ CO	L
5a	29.0 (127)	121.3 [290]	96.1 c)	199.7	171.7 [29]	CH: 146.0 q((19)); Ph: P-C 125.0 m, <i>o</i> -C 134.0 q((3.4)), <i>m</i> -C 131.2 q((2.5)), <i>p</i> -C 134.6
5b ^{d)}		118.1 [291]	85.5		173.7 [30]	CH ₃ : 14.5 br; Ph: 129–131 complex
5c		119.3 [287]	85.8		175.2 [32]	CH: 146.1 q((19)); Ph: P-C 125.2 m, <i>o</i> -C 134.2 q((3.4)), <i>m</i> -C 131.3 q((2.5)), <i>p</i> -C 134.7
5e	29.1	121.3 [289]	96.1	199.8	171.8 [29]	CH ₂ : 29.4 m; Ph: P-C 125.2 m, <i>o</i> -C 135.0 br, <i>m</i> -C 130.8 q((2.5)), <i>p</i> -C 134.7
5f	29.0	b)	96.1	199.8	171.8 [28]	CH: 146.1 m, br; Ph: P-C 124.7 m, <i>o</i> -C 134.2 q((3.4)), <i>m</i> -C 131.1 q((2.5)), <i>p</i> -C 134.6
5g		119.5 [290]	85.9		175.1 [31]	CH ₃ : 14.4 m; Ph: 130–134 complex
5i		b)	85.9		b)	CH: 147.0 m; Ph: P-C 125.1 m, <i>o</i> -C 134.9 q((3.4)), <i>m</i> -C 131.2 q((2.5)), <i>p</i> -C 134.8

a) Chemical shifts in ppm from internal Me_4Si . Figures in parentheses, double parentheses, brackets, and braces give $^1J(\text{C}-\text{H})$, $J(^{31}\text{P}-\text{C})$, $J(^{19}\text{F}-\text{C})$, and $J(^{195}\text{Pt}-\text{C})$ in Hz, respectively. q: quintet, m: multiplet, br: broad.

b) Indiscernible because of low intensity or overlapping with other signals. c) Indiscernible because of the fast H-D exchange with the solvent. d) In CDCl_3 .

TABLE 7. ¹³C NMR DATA FOR $[\text{Pd}(\text{tfac})\text{L}_2](\text{tfac})$ ($\text{L}=\text{PCy}_3$ (**4a**) AND $\text{L}=\text{PPh}_3$ (**4b**)) IN CDCl_3^a

Compd		CH ₃	CF ₃	CH	CH ₃ CO	CF ₃ CO	PCy ₃ ^{e)} or PPh ₃
4a	IS ^{d)}	28.5 ((5;2))	118.5 (9) [284]	96.8 br	194.5 ((2.5))	166.7 [34]	C ^a 34.1 br((19)), 34.2 br((19)); C ^b 27.3 br((9)); C ^r 30.3 br; C ^s 25.8 br P-C 126.1 br((59)), <i>o</i> -C 134.1((11)), <i>m</i> -C 129.0((11)), <i>p</i> -C 132.3
	OS ^{d)}	29.3	120.8 [292]	94.5	197.0	170.1 [28]	
4b ^{e)}		28.4	b)	95.7	196.0	168	

a, b) Same as footnotes for Table 6. c)  d) IS and OS refer to tfac in the inner and outer spheres.

e) Only one set of broad signals for tfac was observed due to the rapid exchange reaction between tfac anions in the inner and outer spheres.

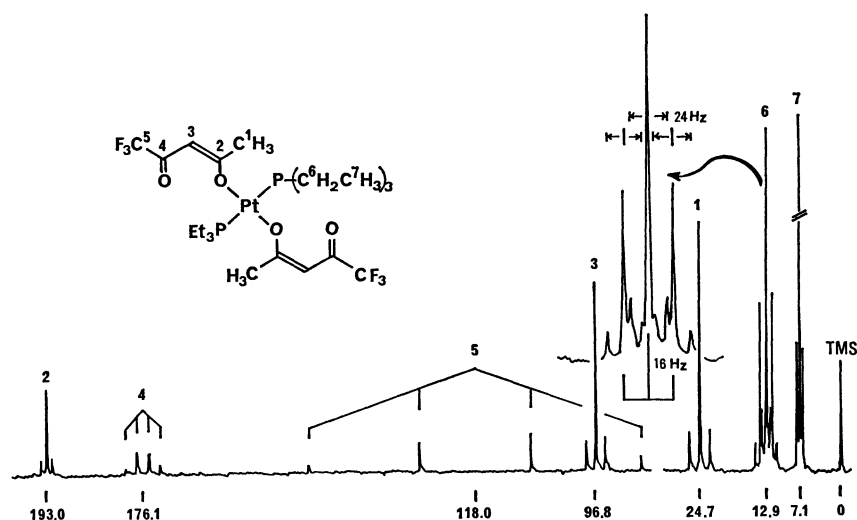


Fig. 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 15.04 MHz of $[\text{Pt}(\text{tfac-O})_2(\text{PEt}_3)_2]$ (**6a**) in CDCl_3 . The $J(\text{Pt-C})$ values are 55, 28, and 55 Hz for CH_3 , CO, and CH of tfac, respectively, and 24 and 15 Hz for CH_2 and CH_3 of PEt_3 , respectively. $^1J(\text{C-F}) = 292$ Hz, $^2J(\text{C-F}) = 31$ Hz.

as large as the $^2J(\text{Pt-C})$ values for CH_3CO and CF_3CO .

Compound **4b** shows one set of carbon signals from $\beta\text{-dik}$, which are broad, sharpening at higher temperature, and their chemical shifts are rough average of those for tfac anions in the inner and outer spheres of **4a** except the CH_3 carbon. The exchange reaction between tfac anions in **4b** is occurring in CDCl_3 solution rapidly on the NMR time scale as was also evidenced by the ^1H NMR spectra (*vide supra*).

Figure 2 displays the $^{13}\text{C}\{^1\text{H}\}$ spectrum of $[\text{Pt}(\text{tfac-O})_2(\text{PEt}_3)_2]$ (**6a**) in CDCl_3 . Each carbon of the CH_3COCH moiety couples to ^{195}Pt ($J = 55$, 28, and 55 Hz, respectively), whereas CF_3 does not, implying that the tfac ligands coordinate to the metal *via* the acetyl oxygen without bonding interaction through CF_3CO . The CH_2 carbon of PEt_3 resonates at 12.9 ppm as a 1:2:1 triplet ($J(\text{P-C}) = 16$ Hz) flanked by ^{195}Pt satellites. Although the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were first thought to provide a powerful tool for determining the stereochemistry of bis(phosphine) metal complexes,¹⁶⁾ later studies have questioned this proposal.¹⁷⁾ Nelson and his collaborators¹⁸⁾ showed that normally the ^{13}C resonances for the *cis* isomers of the square-planar $\text{MX}_2(\text{PR}_3)_2$ type complexes should appear as a quintet, a non 1:2:1 triplet, a doublet of doublets, or a doublet depending on the relative values of $^2J(\text{P-P}')$ and $|^1J(\text{P-C})^3 - J(\text{P}'\text{-C})|^2$, while those for the *trans* isomers with large $^2J(\text{P-P}')$ always appear as 1:2:1 triplets. The 1:2:1 appearance of the CH_2 carbon of PEt_3 in **6a** seems to support the *trans* structure of **6a** in accordance with the ^1H NMR evidence (*vide supra*). The fact that the ^{13}C signals from the O-unidentate tfac ligands in **6a** show no coupling to ^{31}P is also in conformity with the *trans* structure.

The complex $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds **3** were analyzed based on the above-mentioned characteristics of the O-unidentate $\beta\text{-dik}$ and also on the equilibrium ratio of the *cis*(Me,L) and *trans*(Me,L) isomers determined by the ^1H NMR spectroscopy.

As is noticed in Table 8, the difference in the ^{13}C shielding between the two geometrical isomers is more remarkable for the chelated tfac than for the O-unidentate tfac. It seems to be caused by the larger difference in the *trans* influence between the tertiary phosphine and the O-unidentate tfac than that between the CH_3CO and CF_3CO moieties of the chelated tfac ligand.

The ^{13}C NMR data for $[\text{Pd}(\text{bzac})(\text{bzac-C}^2)(\text{PPh}_3)]$ (**7d**) and $[\text{Pd}(\text{tfac})(\text{tfac-C}^3)(\text{PPh}_3)]$ (**7f**), both having unsymmetric $\beta\text{-dik}$, are included in Table 8. Their spectra resemble those of $[\text{M}(\text{acac})(\text{acac-C}^3)(\text{PPh}_3)]$ ($\text{M} = \text{Pd}$ and Pt)⁷⁾ but are more complex due to coexistence of the geometrical isomers. The isomer ratio determined by the ^1H NMR spectroscopy was again helpful in assigning the ^{13}C signals. In a similar manner as the case of compounds **3**, the difference in the ^{13}C shielding between the *cis*(Me,L) and *trans*(Me,L) isomers is more remarkable for the chelated bzac and tfac ligands than for the central-carbon bonded ones. It is worth noting that the carbon-bonded tfac discriminates the geometry of the chelated tfac, whereas the carbon-bonded bzac is insensitive to the configuration of the chelated bzac. Thus the two signals assigned to C^8 of *cis*-**7f** and *trans*-**7f** are 0.5 ppm apart from each other, while C^8 of **7d** resonates as a single peak. The difference in *trans* influence between the CH_3CO and CF_3CO moieties in the chelated tfac seems to be larger than that between the CH_3CO and $\text{C}_6\text{H}_5\text{CO}$ moieties in the chelated bzac.

The Sequence of Reactions between $[\text{M}(\beta\text{-dik})_2]$ and Tertiary Phosphines and Relative Stabilities of Various Products.

Compounds **2–7** in Scheme 1 were obtained by the reactions of $[\text{M}(\beta\text{-dik})_2]$ with tertiary phosphines. When an equimolar amount of PPh_3 was added to a solution of $[\text{Pd}(\text{tfac})_2]$ in CDCl_3 , the ^1H NMR signals attributable to **3b** appeared first prior to those assignable to **7f** which was the final product in this case. Employment of twice molar PPh_3 gave rise to **4b**, which was characterized in solution. Thus,

a, b) Same as footnotes for Table 6. c) The phenyl-ring carbons of bzac and PPh_3 resonate in the 126.5–141.5 ppm region and are indiscernible because of overlapping except the quaternary carbon (C^{10}) of the C-bonded bzac resonating at 141.5 ppm and the ortho carbon of PPh_3 at 134.8 ppm with $^2J(\text{P-C}) = 11 \text{ Hz}$.

compound **7** seems to be formed by a sequence of reactions $1 \rightarrow (2) \rightarrow 3 \rightarrow 4 \rightarrow 7$ as was the case for $[\text{Pd}(\text{acac})(\text{acac}-C^3)\text{Et}_2\text{NH}]$.⁴⁾ The reaction $4 \rightleftharpoons 7$ is reversible and controlled by relative concentrations of the reactants. The five-coordinate complex of the type **2** was not identified for this reaction system, but is presumed to be involved as an intermediate, since stable compound **2** was isolated in the reaction of $[\text{Pd}(\text{hfac})_2]$ with $\text{P}(o\text{-tolyl})_3$.⁵⁾

When *cis*- $[\text{Pt}(\text{tfac})_2]$ was allowed to react with an equimolar amount of PPh_3 , the product was exclusively **3g**, which was converted to **4c** by the reaction with another equivalent of PPh_3 . Similar NMR spectroscopic observation of the reaction sequence was also performed for $[\text{Pt}(\text{acac})(\text{hfac})]$.

Relative stabilities of these ternary complexes are determined by the natures of the metal ion, $\beta\text{-dik}$, and L, and also by the combination of these components. The O-unidentate linkage of $\beta\text{-dik}$ in complexes **3** and **6** seems to be more favorable for Pt(II) than for Pd(II) as suggested by Table 1. For instance, $[\text{Pt}(\text{acac})_2]$ reacts with $\text{P}(o\text{-tolyl})_3$ to yield **3e**, while $[\text{Pd}(\text{acac})_2]$ does not. Both of $[\text{M}(\text{tfac})_2]$ ($\text{M} = \text{Pt}$ and Pd) react with equimolar PCy_3 to produce compounds **3**, but the succeeding reactions with another mole of PCy_3 give rise to **6b** in the Pt(II) case, while to **4a** in the Pd(II) case. It is noteworthy that Pd(II) prefers $[\text{Pd}(\text{tfac})(\text{PCy}_3)_2](\text{tfac})$ (**4a**) over the *trans*- $[\text{Pd}(\text{tfac}-O)_2(\text{PCy}_3)_2]$ structure in spite of the mutual steric hindrance of the two PCy_3 ligands at the *cis* positions in **4a**.

The central carbon bonding in **7** is much more favorable for Pd(II) than for Pt(II). Thus the reaction of PEt_3 with $[\text{Pd}(\text{acac})_2]$ gives **7a** exclusively, whereas that with $[\text{Pt}(\text{acac})_2]$ results only in $[\text{Pt}(\text{acac}-O)_2(\text{PEt}_3)_2]$.⁶⁾ In the reactions of $[\text{M}(\text{acac})_2]$ with secondary amines, Pd(II)^{2a)} gave complexes of types **4** and **7**, while Pt(II)^{2b)} **4** and **6**. On the other hand, $[\text{Pt}(\text{acac})_2]$ was reported to produce $[\text{Pt}(\text{acac}-C^3)_2(\text{py})_2]$ besides $[\text{Pt}(\text{acac})(\text{acac}-C^3)(\text{py})]$,¹⁹⁾ but $[\text{Pd}(\text{acac})_2]$ gave only the latter type-**7** complex.^{1a)} Platinum looks to prefer carbon bonding with acac more strongly than palladium does in this $[\text{Pd}(\text{acac})_2]\text{-py}$ system, although reasonable rationalization is difficult.

As to the role of $\beta\text{-dik}$, the basicity is the most important factor. Thus the reactivity of $[\text{Pd}(\beta\text{-dik})_2]$ with nitrogen bases was in the sequence $\text{acac} < \text{tfac} < \text{hfac}$, half preferring most strongly to go out of the coordination sphere.²⁾ Similar trend is also observed for reactions with less bulky tertiary phosphines (Table 1). The type-**2** complexes were obtained only from $[\text{M}(\text{hfac})_2]$ whose acidity may be the highest among the $[\text{M}(\beta\text{-dik})_2]$ complexes due to the lowest basicity of hfac.

The unsymmetric tfac anion seems to stabilize the O-unidentate linkage as compared with acac, giving many kinds of compounds of the **3** and **6** types. On the other hand, $[\text{M}(\text{acac})_2]$ gave **7** by the reactions with phosphines^{1a,7)} except $\text{P}(o\text{-tolyl})_3$ and PEt_3 which reacted with $[\text{Pt}(\text{acac})_2]$ to afford **3e** and the type-**6** complex,⁶⁾ respectively. The central carbon bonding is more favorable for acac than for tfac and hfac. Ito and Yamamoto²⁰⁾ examined the reactions of $[\text{Pt}$ -

$(\text{acac})(\text{acac}-C^3)(\text{PPh}_3)]$ with several $\beta\text{-dicarbonyl}$ compounds ($\beta\text{-dikH}$) in refluxing toluene and found that the keto-favoring $\beta\text{-dikH}$ could replace the carbon-bonded acac more easily.

The reactions of $[\text{M}(\text{acac})(\beta\text{-dik})]$ with phosphines clearly distinguish the labilities of the $\beta\text{-dik}$ ligands. The tfac or hfac chelate is preferentially cleaved firstly, the acac chelate being preserved intact. Complexes **3** and **4** derived from the mixed ligand chelates seem to be more stable than those from the binary chelates. The acac ligand preferring the chelated state and tfac which is suitable as the unidentate ligand or counter anion may cooperate to stabilize **3** and **4**.

The σ -basicity of tertiary phosphines was deduced from the frequency of the A_1 carbonyl mode of $\text{Ni}(\text{CO})_3\text{L}$ in CH_2Cl_2 to be in the sequence,¹³⁾ $\text{PCy}_3 > \text{PEt}_3 > \text{PMe}_2\text{Ph} > \text{P}(o\text{-tolyl})_3 > \text{PMePh}_2 > \text{PPh}_3$. The fact that the reaction of $[\text{Pt}(\text{acac})_2]$ with PPh_3 gives **7**,⁷⁾ whereas that with PEt_3 results solely in **6**⁶⁾ seems to reflect the electronic effect of phosphines on the choice of the bonding mode of $\beta\text{-dik}$ ligands. In complexes **7**, less σ -basic and more π -acidic triarylphosphines will diminish the charge density on the metal atom, strengthening the bond with strong σ -donors such as the carbon-bonded $\beta\text{-dik}$. On the other hand, strongly σ -basic trialkylphosphines will prefer the O-unidentate $\beta\text{-dik}$ which is a weak σ -donor to the carbon-bonded one, stabilizing complexes **6**.

The steric effect of tertiary phosphines is more remarkable. For example, $\text{P}(o\text{-tolyl})_3$ can convert only one of the chelating ligands in $[\text{M}(\beta\text{-dik})_2]$ into the O-unidentate state to result in complexes **3**, but can not give succeeding products. Bulky $\text{P}(o\text{-tolyl})_3$ (cone angle 194°)¹³⁾ in the coordination sphere might prevent attack of the second phosphine molecule on the central metal in both the kinetic and thermodynamic senses. On the other hand, PPh_3 (cone angle 145°)¹³⁾ can conduct reactions to give $3 \rightarrow 4 \rightarrow 7$. Less bulky PMe_2Ph (122°) and dppe (125°)¹³⁾ afford complexes **5** although the electronic factor might also be favorable.

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