

# Reactions of *Bis*(Pivaloyl Trifluoroacetato) Palladium(II) with Lewis Bases

B. K. SAHU\* and B. K. MOHAPATRA

Department of Chemistry, B. J. B. College, Bhubaneswar-14

Manuscript received 27 April 1982, accepted 28 December 1982

Reactions of *bis*(pivaloyl trifluoroacetato)palladium(II) with a number of bases produced compounds of the type  $[PdL_2]X_2$ ,  $[PdL'_2(X)]X$ ,  $[PdL''(X)]X$  and  $[Pd(X)(\gamma-X)L''']$  where X is the anion of pivaloyl trifluoroacetone, L = pyridine,  $\beta$ -picoline,  $\gamma$ -picoline, 3,5-lutidine, L' = piperidine, L'' = bipyridine and L''' =  $\alpha$ -picoline, 2,6-lutidine or triphenyl phosphine. These have been characterised on the basis of analyses and infrared and pmr spectral data.

$\beta$ -DIKETONES are versatile ligands, the anion of which coordinates with metal ions forming O,O'-chelate<sup>1</sup>. Central carbon bonded acetylacetonate complexes of palladium(II) and platinum(II) have been reported<sup>2-4</sup> by reacting  $Pd(ac.ac)_2$  and  $Pt(ac.ac)_2$  with various bases. Central carbon bonded ionic platinum(II) acetylacetonato complex was reported by Lewis<sup>5</sup> *et al* and its reaction with metal salts in aqueous media produced complexes of the type  $M[PtCl(ac.ac)_2]_2^{6,7}$ . A terminal carbon bonded acetylacetonato complex has been prepared<sup>8</sup>. We have been studying the various linkage modes of  $\beta$ -diketones in transition metal complexes. Reactions of central and terminal carbon bonded palladium(II) acetylacetonate<sup>9</sup> and central carbon bonded platinum(II) acetylacetonate complex with other  $\beta$ -diketones have been reported by us<sup>10</sup>. Reactions of several palladium(II)  $\beta$ -diketonate complexes with various nitrogen bases have also been studied<sup>11</sup> by us. As a part of this programme this communication reports the reactions of *bis*(pivaloyl trifluoroacetato)palladium(II) with a number of Lewis bases.

## Experimental

Aqueous solution of  $K_2PdCl_4$  was magnetically stirred with ethanolic solution of pivaloyl trifluoroacetone in 1 : 2 molar proportion. To this, twice molar sodium acetate solution was added drop by drop and the stirring continued for another 1 hr after addition was completed. The yellow precipitate was filtered off, dried in vacuum and extracted with dichloromethane. Volume of the filtrate was reduced in a rotary vacuum evaporator to produce yellow crystals, which were subsequently recrystallised from dichloromethane-petroleum ether, yield = 65%.

0.25 g of *bis*(pivaloyl trifluoroacetato)palladium(II) was suspended in 3 ml of different liquid bases separately and stirred at 40° for 30 min to produce a clear solution. The solution was kept in

a refrigerator overnight when yellow crystalline compounds separated out. These were recrystallised from dichloromethane-petroleum ether, yield 80-85%. In case of  $\alpha$ -picoline or 2,6-lutidine as base, a brown oily substance was produced on evaporation which was repeatedly digested with small amounts of dichloromethane and petroleum ether and kept in refrigerator to afford yellow powder. In case of triphenylphosphine and bipyridine the chelate was stirred with 1 : 1 molar proportion of base in 20 ml of dichloromethane and the solvent was reduced to 5 ml which on keeping in refrigerator gave a brown oil. It was worked up in a similar manner to produce yellow powder.

Composition of the complexes was determined by C, H, N microanalyses. Molar conductance was measured in  $10^{-3}M$  acetone solution using a Toshniwal conductance bridge. Infrared spectra were recorded on Perkin-Elmer 621 and 337 spectrophotometers. PMR spectra were recorded in  $CDCl_3$  solution by a JEOL JNM 100 MHz spectrophotometer using tetramethyl silane as an internal reference. The analytical data are presented in Table 1 and the spectral data in Table 2.

## Results and Discussion

All the complexes reported are either yellow crystals or powder. Molar conductance data show complex Nos. 1, 2, 3 and 6 to be 1 : 2 electrolytes, 4, 5 to be 1 : 1 electrolytes and 7, 8 and 9 to be non-electrolytes. The analysis shows that the complexes have the composition  $PdL_2X_2$ ,  $PdL'_2X_2$ ,  $PdL''X_2$  and  $PdL'''X_2$  where L is pyridine,  $\beta$ -picoline,  $\gamma$ -picoline or 3,5-lutidine, L' is piperidine, L'' is bipyridine, L''' is triphenyl phosphine,  $\alpha$ -picoline, 4-cyano pyridine or 2,6-lutidine and X is the anion of pivaloyl trifluoroacetone.

Infrared spectra of  $Pd(pta)_2$  show bands at 1580, 1535, 1515  $cm^{-1}$  attributable to  $\nu(C=O) + \nu(C=C=C)$  modes. In the reaction products of

\*Permanent Address : Anandpur College, Anandpur, Keonjhar, Orissa.

TABLE 1—ANALYTICAL DATA

Compounds	Colour and form	Analysis%			$\Delta_M$ (mhos.cm <sup>2</sup> ) in acetone
		C	H	N	
1. [Pd(py) <sub>4</sub> ](pta) <sub>2</sub>	Yellow crystals	52.96 (53.15)*	4.72 (4.92)	6.80 (6.99)	205
2. [Pd( $\beta$ -pic) <sub>4</sub> ](pta) <sub>2</sub>	"	55.01 (55.25)	5.48 (5.53)	6.39 (6.45)	200
3. [Pd( $\gamma$ -pic) <sub>4</sub> ](pta) <sub>2</sub>	"	55.02 (55.25)	5.46 (5.53)	6.38 (6.45)	208
4. [Pd(pta)(bpy)](pta)	"	47.71 (47.80)	4.08 (4.29)	4.05 (4.29)	130
5. [Pd(pta)(pipe) <sub>2</sub> ](pta)	"	46.67 (46.77)	5.62 (5.60)	4.25 (4.20)	124
6. [Pd( $\beta$ , $\delta$ -lut) <sub>4</sub> ](pta) <sub>2</sub>	"	57.19 (57.10)	5.92 (6.06)	5.95 (6.06)	215
7. [Pd(pta)( $\gamma$ -pta)(Ph <sub>2</sub> P)]	"	53.72 (53.75)	4.55 (4.61)	—	10.5
8. [Pd(pta)( $\gamma$ -pta)( $\alpha$ -pic)]	"	44.67 (44.77)	4.51 (4.58)	2.25 (2.37)	8.8
9. [Pd(pta)( $\gamma$ -pta)(2,6-lut)]	"	45.66 (45.71)	4.68 (4.80)	2.22 (2.32)	10.8
10. [Pd(pta)( $\gamma$ -pta)(4-CN.py)]	Light yellow cryst.	43.84 (43.95)	4.1 (4.0)	4.71 (4.65)	8.6

\* Calculated values are in parentheses.

pta = anion of pivaloyl trifluoroacetone, py = pyridine, pip = piperidine, lut = lutidine, bpy = bipyridine,  $\beta/\gamma$ -pic =  $\beta/\gamma$ -picoline, 4CNpy = 4-cyano pyridine,  $\gamma$ -pta = central carbon bonded pivaloyl trifluoroacetone.

TABLE 2—INFRARED SPECTRA (cm<sup>-1</sup>) AND PMR SPECTRA  $\delta$  (ppm)

Compounds	$\nu(\text{C=O}) + \nu(\text{C=C})$		C-bonded pta	CH ionic pta	CH O-bonded pta	CH C-bonded pta
	O-bonded pta	Ionic pta				
1.	—	1635	—	5.34	—	—
2.	—	1630	—	5.38	—	—
3.	—	1635	—	5.28	—	—
4.	1590, 1535, 1515	1630	—	5.32	5.78	—
5.	1590, 1535, 1520	1630	—	5.28	5.76	—
6.	—	1635	—	5.32	—	—
7.	1590, 1530, 1515	—	1710	—	5.82	5.04
8.	1590, 1535, 1520	—	1710	—	5.78	5.02
9.	1600, 1530, 1520	—	1715	—	5.78	4.98
10.	1590, 1535, 1515	—	1710	—	5.76	4.98

bases carbonyl stretching bands appear in three different regions. PdL<sub>4</sub>X<sub>2</sub> type complexes show the  $\nu(\text{C=O})$  band in the 1635-1638 cm<sup>-1</sup> region which can be assigned to the ionic pivaloyl trifluoroacetate (pta) group. PdL'<sub>2</sub>X<sub>2</sub> and PdL''X<sub>2</sub> have the carbonyl bands in the 1590 and 1630 cm<sup>-1</sup> region, the former is attributed to the chelating pta and the latter to the ionic pta group. In PdL''X<sub>2</sub> type of complexes carbonyl stretching vibration appears at 1590 and 1710-1715 cm<sup>-1</sup> region. The former band can be assigned to the chelated pta and the latter to the  $\gamma$ -carbon bonded pta group in analogy with many earlier observations on  $\beta$ -diketonate complexes. In conformity with the molar conductance data complex Nos. 1, 2, 3 and 6 have the structure [PdL<sub>4</sub>]X<sub>2</sub> where both the pta groups are ionic and outside the coordination sphere. Complex Nos. 4 and 5 contain one chelated pta and another ionic pta group and complex Nos. 7, 8, 9 and 10 contain one O,O'-chelated pta group and another  $\gamma$ -carbon (central carbon) bonded pta group.

Study of the pmr spectra of Pd(pta)<sub>2</sub> and other complexes corroborates this type of structure of the compounds. In Pd(pta)<sub>2</sub> methine proton of chelated pta group resonates at 5.8 ppm and methyl protons at 1.2 ppm. [PdL<sub>4</sub>]X<sub>2</sub> type of complexes show methine proton signal around 5.28-5.38 ppm due to the presence of ionic pta group. [PdL'<sub>2</sub>X]X and [PdL''X]X type of compounds have methine proton signals around 5.28-5.32 ppm and 5.76-5.78 ppm. The former signal is attributed to the ionic pta group and the latter to the chelated pta. Thus, the presence of one chelated pta and one ionic pta group in these type of compounds is confirmed. In case of complexes of the type [PdL(pta)( $\gamma$ -pta)] methine protons resonate at 5.76-5.82 ppm and 4.98-5.04 ppm. The former signal is assigned to the chelated pta group and the latter to the  $\gamma$ -carbon (central carbon) bonded pta group. PMR assignments have been done on the basis of many earlier observations<sup>11-14</sup> on the chelated, ionic and  $\gamma$ -carbon bonded  $\beta$ -diketonate groups.

#### Acknowledgement

Thanks of the authors are due to Prof. Shinichi Kawaguchi, Osaka City University, Osaka, Japan for initiating our interest in the reactions of palladium(II), platinum(II)  $\beta$ -diketonate complexes while one of us (B. K. M.) was working as a J. S. P. S. Visiting Fellow.

#### References

1. J. P. FACKLER, JR., *Progr. Inorg. Chem.*, 1966, 7, 361.
2. S. BABA, T. OGURA and S. KAWAGUCHI, *Bull. Chem. Soc. Japan*, 1974, 47, 665.
3. T. ITO, T. KIRIYAMA, Y. NAKAMURA and A. YAMAMOTO, *Bull. Chem. Soc. Japan*, 1976, 49, 3257.

- 4 B. K. SAHU and B. K. MOHAPATRA, *J. Indian Chem Soc.*, 1981, **58**, 731.
- 5 B. N. FIGGIS, J. LEWIS, R. F. LONG, R. MASON, R. S. NYHOLM, P. J. PAULING and G. ROBINSON, *Nature*, 1962, **195**, 1278
- 6 J. LEWIS and C. OLDHAM, *J. Chem. Soc. A*, 1966, 1456
- 7 Y. NAKAMURA and K. NAKAMOTO, *Inorg. Chem.*, 1975 **14**, 68.
- 8 Z. KANDA, Y. NAKAMURA and S. KAWAGUCHI, *Inorg Chem.*, 1978, **17**, 910.
- 9 B. K. SAHU and B. K. MOHAPATRA, *J. Inorg Nuclear Chem.*, Communicated.
- 10 B. K. SAHU and B. K. MOHAPATRA, *Acta Chimica* Accepted
- 11 S. OKEYA, S. SAZAKI, M. OGITA, T. TAKAMOTO, Y. ONUKI, Y. NAKAMURA, B. K. MOHAPATRA and S. KAWAGUCHI, *Bull. Chem Soc Japan*, 1981, **54**, 1978
- 12 S. OKEYA, Y. ONUKI, Y. NAKAMURA and S. KAWAGUCHI, *Chem Lett. Japan*, 1977, 1305
- 13 S. OKEYA and S. KAWAGUCHI, *Inorg. Chem*, 1977, **16**, 1730
- 14 T. ITO and A. YAMAMOTO, *J. Organometal Chem*, 1979, **174**, 237