Preparation of $Ph_2PC_5H_4$- and $PhP(C_5H_4)_2$-Bridged Zirconium(IV)–Platinum(II) Complexes

GORDON K. ANDERSON* and MINREN LIN

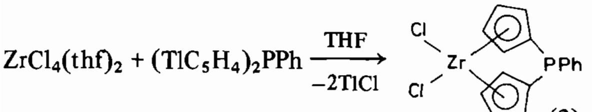
Department of Chemistry, University of Missouri-St. Louis, St. Louis, Mo. 63121, U.S.A.

(Received July 20, 1987)

There has been considerable interest recently in the synthesis of heterometallic complexes, but relatively few examples have been prepared that contain an early transition metal (d^0) and a d^8 or d^{10} metal [1–7]. Phosphido-bridged Zr(IV)–Pt(O) species have been obtained by reaction of $(C_5H_5)_2Zr(PPh_2)_2$ with $Pt(PPh_3)_4$, and subsequent reactions involving substitution of PPh_3 [7], but no Zr(IV)–Pt(II) complexes have been reported. We describe here the preparation of $Ph_2PC_5H_4$- and $PhP(C_5H_4)_2$-bridged compounds containing a platinum(II) and one or two zirconium(IV) centers.

We have prepared (diphenylphosphino)cyclopentadienylthallium according to the method of Rausch *et al.* [8], and used this reagent in a modified synthesis of $Cl_2Zr(C_5H_4PPh_2)_2$ [9]. We have also generated the related zirconium compound, $Cl_2Zr(C_5H_4)_2PPh$, according to eqns. (1) and (2), as a light yellow powder in 78% overall yield. The two zirconium compounds exhibit ^{31}P NMR resonances at −17.2 and −28.9 ppm respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectra of $Cl_2Zr(C_5H_4PPh_2)_2$ are unremarkable, but the C_5H_4 units in $Cl_2Zr(C_5H_4)_2PPh$ give rise to four ^1H and five ^{13}C resonances, indicating that, whereas the two rings are equivalent, there is a source of asymmetry in the molecule which renders all five ring carbons magnetically non-equivalent. This is perhaps not surprising in view of the steric strain which must be inherent in the molecule. This spectroscopic phenomenon persists when the phosphorus atom is coordinated to platinum.

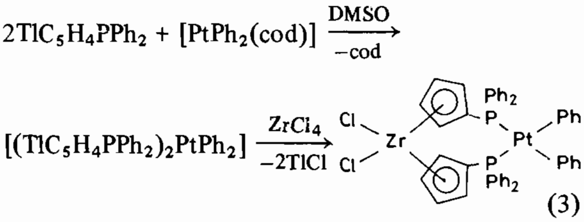
$$2C_5H_5Tl + Cl_2PPh \xrightarrow[-2TlCl]{Et_2O} (C_5H_5)_2PPh \xrightarrow[-2EtOH]{2TlOEt} (TlC_5H_4)_2PPh \qquad (1)$$



(2)

$$ZrCl_4(thf)_2 + (TlC_5H_4)_2PPh \xrightarrow[-2TlCl]{THF}$$

When $Cl_2Zr(C_5H_4PPh_2)_2$ is added slowly to a CH_2Cl_2 solution of $[PtPh_2(cod)]$ an orange color develops and, upon solvent removal and washing with petroleum ether, $[Cl_2Zr(C_5H_4PPh_2)_2PtPh_2]$ is obtained as an orange solid. This complex may be prepared alternatively by first attaching the phosphino groups to platinum, followed by reaction with $ZrCl_4$ (eqn. (3)). The intermediate complex, $[(TlC_5H_4PPh_2)_2PtPh_2]$ (δP 10.4, ^1J(Pt,P) 1840 Hz), is of *cis*-geometry, as is the final product. Addition of $Cl_2Zr(C_5H_4PPh_2)_2$ to a CH_2Cl_2 solution of $[PtClPh(cod)]$ produces a yellow solution, from which $[Cl_2Zr(C_5H_4PPh_2)_2PtClPh]$ is isolated as a white powder. This complex is also of *cis*-geometry, as evidenced by the non-equivalence of the two phosphorus atoms (Table I).



(3)

$$2TlC_5H_4PPh_2 + [PtPh_2(cod)] \xrightarrow[-cod]{DMSO} [(TlC_5H_4PPh_2)_2PtPh_2] \xrightarrow[-2TlCl]{ZrCl_4}$$

TABLE I. $^{31}P\{^1H\}$ NMR Data for the Zr(IV)–Pt(II) Complexes

Complex	δP[a]	^1J(Pt,P) (Hz)
$Cl_2Zr(C_5H_4PPh_2)_2PtPh_2$	13.5	1750
$Cl_2Zr(C_5H_4PPh_2)_2PtClPh$	13.2[b]	1523
	12.1[b]	4428
$[Cl_2Zr(C_5H_4)_2PPh]_2PtPh_2$	−1.7	1725
$[Cl_2Zr(C_5H_4)_2PPh]_2PtClPh$	5.2	3247

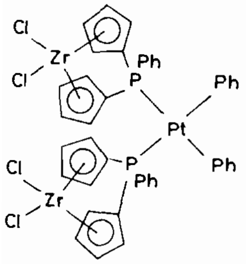
[a] Chemical shifts are in ppm relative to external H_3PO_4, positive shifts representing deshielding. [b] ^2J(P,P) 17 Hz.

Slow addition of 0.5 mol equiv. of $[PtPh_2(cod)]$ to a THF solution of $Cl_2Zr(C_5H_4)_2PPh$, followed by solvent removal and washing with petroleum ether, gives $[\{Cl_2Zr(C_5H_4)_2PPh\}_2PtPh_2]$ as an analytically pure, light yellow powder in 80% yield. Similarly, reaction of $[PtClPh(cod)]$ with $Cl_2Zr(C_5H_4)_2PPh$ yields $[\{Cl_2Zr(C_5H_4)_2PPh\}_2PtClPh]$ as a light yellow solid in 83% yield. The small ^1J(Pt,P) value indicates that the diphenylplatinum complex **(A)** is of *cis*-geometry (Table I), whereas the magnetic equivalence of the phosphorus atoms in $[\{Cl_2Zr(C_5H_4)_2PPh\}_2PtClPh]$ demonstrates that they are in mutually *trans* positions **(B)**.

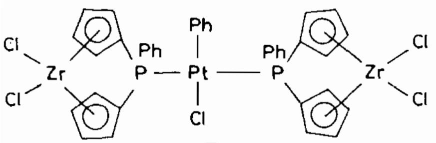
---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50



A



B

Thus the $Cl_2Zr(C_5H_4PPh_2)_2$ ligand is apparently able to span two *cis*-positions only, whereas the monodentate $Cl_2Zr(C_5H_4)_2PPh$ allows the chloro(phenyl)platinum moiety to adopt the preferred *trans*-geometry. We are presently investigating the effect of the presence of the Zr(IV) center(s) on the reactivity of the Pt–Ph bonds towards carbonyl insertion and related reactions.

Acknowledgements

Thanks are expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Missouri Weldon Spring Fund for support of this work, and to Johnson Matthey for a generous loan of platinum salts.

References

1 N. E. Schore and H. Hope, *J. Am. Chem. Soc., 102,* 4251 (1980).
2 R. Choukroun and D. Gervais, *J. Chem. Soc., Chem. Commun.,* 1300 (1982); *J. Organomet. Chem., 266,* C37 (1984); M. Etienne, R. Choukroun, M. Basso-Bert, F. Dahan and D. Gervais, *Nouv. J. Chemie, 8,* 431 (1984); F. Senocq, M. Basso-Bert, R. Choukroun and D. Gervais, *J. Organomet. Chem., 297,* 155 (1985).
3 J. C. Leblanc, C. Moise, A. Maisonnat, R. Poilblanc, C. Charrier and F. Mathey, *J. Organomet. Chem., 231,* C43 (1982).
4 R. T. Baker, T. H. Tulip and S. S. Wreford, *Inorg. Chem., 24,* 1379 (1985); R. T. Baker and T. H. Tulip, *Organometallics, 5,* 839 (1986).
5 G. S. White and D. W. Stephan, *Inorg. Chem., 24,* 1499 (1985); T. A. Wark and D. W. Stephan, *Inorg. Chem., 26,* 363 (1987).
6 G. S. Ferguson and P. T. Wolczanski, *Organometallics, 4,* 1601 (1985).
7 L. Gelmini and D. W. Stephan, *Inorg. Chim. Acta, 111,* L17 (1986); *Inorg. Chem., 25,* 1222 (1986).
8 M. D. Rausch, B. H. Edwards, R. D. Rogers and J. L. Atwood, *J. Am. Chem. Soc., 105,* 3882 (1983).
9 W. Tikkanen, Y. Fujita and J. L. Petersen, *Organometallics, 5,* 888 (1986).