solution with $Rh_2(CO)_4Cl_2$ in dichloromethane to give the known[9] $CoRh(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2(\mu\text{-Cl})]Cl$ (9) in 43% yield. Further such studies are in progress.

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Supplementary Material Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for 1 and ORTEP diagrams of 1 (5 pages); a listing of structure factors for 1 (20 pages). Ordering information is given on any current masthead page.

Notes

Imine-Transfer Reactions from Zirconium to Phosphorus and Boron. Synthesis of the First *C*-Phosphanyl-, *N*-Phosphanyl-, or *N*-Boranylimines

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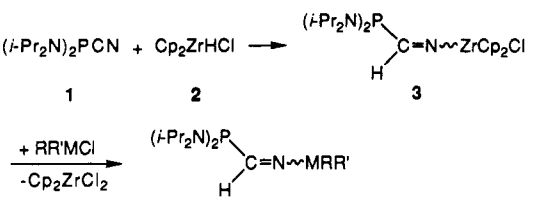
Summary: A "one-pot" reaction involving $(i\text{-Pr}_2N)_2PCN$ (**1**), the Schwartz reagent Cp_2ZrHCl (**2**), and halogenated phosphorus or boron species allows the synthesis of the first *C*-phosphanyl-, *N*-phosphanyl-, or *N*-boranylimines, **4–8**.

Organozirconium reagents have found widespread application in organic synthesis but less frequently in main-group element chemistry.[1] Our continuing interest in this area is to develop new routes to functionalized organic derivatives possessing one or more main-group elements. We have already provided examples of unusual neutral or cationic metallacycles obtained via hydrozirconation[2] of analogous phosphorus compounds of alkenes or imines, i.e., phospha-alkenes R—P=C< or iminophosphanes R—P=N–.

Here we report the use of the readily available *N*-zirconium–imino compound **3** for the facile preparation of the first *N*- and *C*-diphosphanyl- or *C*-phosphanyl-*N*-boranylimines, **4–6** or **7** and **8**. Until now only diphosphorylated species **9**, in which the two phosphorus atoms are tetracoordinated, were known.[3]

The *N*-zirconium–imino species **3** was conveniently prepared in near-quantitative yield by reacting bis(diisopropylamino)cyanophosphane (**1**)[4] with Cp_2ZrHCl (**2**) in THF.[5] Evidence for the formation of **3** was mainly given by ^1H NMR (δ C*H*=N 9.66 ppm (d, $^2J_{PH}$ = 60.0 Hz)) and ^{13}C NMR spectroscopy (δ(*C*=N) 184.56 ppm (d, $^1J_{CP}$ = 13.7 Hz)).



4, M = P, R = R' = Ph
5, M = P, R = *i*-Pr$_2$N, R' = Cl
6, M = P, R = R' = *i*-Pr$_2$N
7, M = B, R = R' = *i*-Pr$_2$N
8, M = B, R = NSiMe$_3$N(SiMe$_3$)$_2$, R' = Cl
12, MRR' = SnMe$_3$

We have demonstrated that derivative **3** is a useful starting reagent for the synthesis of a large variety of *C*-phosphanyl–imines. Thus, treatment of **3** (0.295 g, 0.570 mmol) in THF (8 mL) at –40 °C with Ph_2PCl (0.126 g, 0.570 mmol) resulted in an immediate reaction. After removal of the solvent, the resulting powder was extracted with pentane (2 × 5 mL) to afford **4** (70% yield). The structure of **4** was deduced from ^1H, ^{13}C, and ^{31}P NMR as well as IR and mass spectrometry and elemental analysis. For example, the imino carbon signal appeared as a doublet of doublets ($^1J_{CP}$ = 24.7 Hz, $^2J_{CP}$ = 4.0 Hz) centered at 178.21 ppm in the ^{13}C NMR spectrum, while a doublet of doublets at 8.62 ($^2J_{HP}$ = 56.7 Hz, $^3J_{HP}$ = 29.9 Hz) ppm was observed for the imino proton in the ^1H NMR spectrum. Lastly, the ^{31}P NMR spectrum exhibited two doublets (δ = 56.5 and 60.6 ppm, $^2J_{PP}$ = 26.2 Hz) corroborating the presence of two different phosphane groups.

The iminodiphosphane **5** was similarly prepared from **3** and (diisopropylamino)dichlorophosphane $(i\text{-Pr}_2N)PCl_2$.

† UP 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique.

(1) See for example: (a) Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537. (b) Muklenbernd, T.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 1023. (c) Heisteeg, B. J. J.; Schat, G.; Akkermann, O. S.; Bickelhaupt, F. *Organometallics* **1986**, *5*, 1749. (d) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (e) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1988**, *53*, 4425. (f) Buchwald, S. L.; Fisher, R. A.; Foxman, B. M. *Angew. Chem., Int. Engl.* **1990**, *29*, 771. (g) Fisher, R. A.; Nielsen, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 165–171.

(2) Dufour, N.; Majoral, J.-P.; Caminade, A.-M.; Choukroun, R.; Dromzee, Y. *Organometallics* **1991**, *10*, 45. Majoral, J.-P.; Dufour, N.; Meyer, F.; Caminade, A.-M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1990**, 507.

(3) Levkova, L. N.; Alimov, P. I. *Izv. Akad. Nauk SSSR, Ser. Khim* **1966**, *12*, 2218.

(4) Roques, C.; Mazières, M. R.; Majoral, J.-P.; Sanchez, M.; Foucaud, A. *J. Org. Chem.* **1989**, *54*, 5535.

(5) (a) Hydrozirconation of *p*-tolunitrile with $Cp^*_2ZrH_2$ has been reported to provide the azomethine insertion product: Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (b) Hydrozirconation of R—C≡N (R = CH_3, C_6H_5, $CH_2C_6H_5$) with Cp_2ZrHCl led to formation of the corresponding metalla-imines: Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343.

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An analogous reaction with the more sterically crowded bis(diisopropylamino)chlorophosphane $(i\text{-Pr}_2\text{N})_2\text{PCl}$ required stirring for 36 h to generate the expected compound **6**.

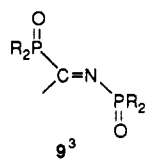
Surprisingly, **6** was also obtained by treatment of **3** with (trimethylsilyl)trifluoromethanesulfonate. This reaction involves an unusual phosphorus–carbon bond cleavage with subsequent transfer of the $(i\text{-Pr}_2\text{N})_2\text{P}$ moieties.

The *C*-phosphanyl–imino unit can also be transferred from zirconium to boron. The addition of bis(diisopropylamino)chloroborane, $(i\text{-Pr}_2\text{N})_2\text{BCl}$, or tris(trimethylsilyl)hydrazinodichloroborane, $(\text{Me}_3\text{Si})_2\text{NN(SiMe}_3)\text{BCl}_2$,[6] in the same way as described for phosphine chlorides, generated the corresponding *C*-phosphanyl-*N*-boranylimines **7** and **8** in excellent isolated yield.

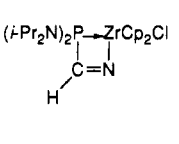
To our knowledge such reactions leading to new main-group element substituted imines have not previously been achieved. The zirconium imine **3** need not to be isolated, and "one-pot" syntheses can be carried out in all cases.

Depending on the experimental conditions, small amounts (as indicated by ^{31}P NMR analysis) of cyanophosphane $(i\text{-Pr}_2\text{N})_2\text{PCN}$ were formed during the reaction involving **3** and halogenated phosphorus or boron compounds, pointing out the possibility of an equilibrium—largely displaced toward **3**–between **3** and the starting reagents $(i\text{-Pr}_2\text{N})_2\text{PCN}$ and Cp_2ZrHCl.

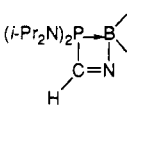
The fact that ^{31}P chemical shifts of the *C*-phosphanyl part of the molecules **3**, **4–6**, **7** and **8** are very close (between 56.2 and 61.2 ppm) might suggest a trans conformation for these derivatives, the hydrozirconation of the cyanophosphane **1** being cis, as expected. Indeed, no evidence has been found for the formation of the unsaturated four-membered rings **10** or **11**: NMR studies showed no resolvable coupling between phosphorus and protons of the Cp groups in **3**, and there was no deshielding effect in the ^{31}P NMR spectrum due to dative bond P→Zr or P→B.[2]



9[3]



10

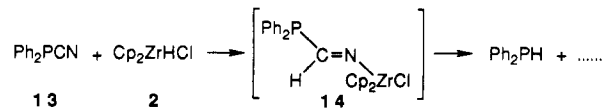


11

R= aryl, aryloxy, or alcoxy groups.

The phosphanyl–imino transfer also seems to operate in other metalloid systems. For example, addition of Me_3SnCl to **3** afforded the corresponding unstable phosphorus tin imine **12** ($\delta(^{119}\text{Sn}) = 115.2$ ppm), which can be trapped with Ph_2PCl to give the imine **4**.

Hydrozirconation of diphenylcyanophosphane **13** led to the very unstable *C*-phosphanyl-*N*-zirconia-imine **14** which can be detected by ^{31}P NMR spectroscopy ($\delta(^{31}\text{P}) = 0.04$ ppm, $^2J_{\text{PH}} = 48.7$ Hz) but cannot be isolated: this compound quickly rearranged to give the diphenylphosphane Ph_2PH as the major product.



13 **2** **14**

These highly functionalized imines are now being evaluated in organic synthesis as well as in coordination chemistry and catalysis.

(6) Brodie, N.; Majoral, J.-P. Unpublished results.

Experimental Section

General Considerations. All manipulations were carried out under a dry and oxygen-free atmosphere of argon by using standard Schlenk techniques. NMR spectra were recorded on a Brucker AC 80 or AC 200 spectrometer and referenced as follows: ^{31}P, external 85% H_3PO_4; ^1H and ^{13}C, external TMS; ^{11}B, external $\text{BF}_3\cdot\text{OEt}_2$; ^{119}Sn, external Me_4Sn. IR spectra were recorded on a Beckman IR 10 spectrometer. Mass spectra were obtained on a Ribermag R10 10E spectrometer. Microanalyses were conducted at the laboratory. Solvents and reagents were purified as follows: THF distilled from Na/benzophenone; pentane distilled from sodium; C_6D_6 distilled over CaH_2 and stored over molecular sieves 3 Å; Ph_2PCl (Aldrich) and Me_3SnCl (Aldrich) used as received. Cp_2ZrHCl,[7] $(i\text{-Pr}_2\text{N})_2\text{PCl}$,[8] $(i\text{-Pr}_2\text{N})_2\text{PCN}$,[4] Ph_2PCN,[9] and $(i\text{-Pr}_2\text{N})_2\text{BCl}$[10] were prepared by literature procedures.

Preparation of $(i\text{-Pr}_2\text{N})_2\text{PC(H)=NZrCp}_2\text{Cl}$ (3). A solution of cyanophosphine $(i\text{-Pr}_2\text{N})_2\text{PCN}$ (**1**) (0.566 g, 2.20 mmol) in THF (10 mL) was added dropwise to an heterogeneous mixture of Cp_2ZrHCl (**2**) (0.567 g, 2.20 mmol) in THF (10 mL) at room temperature. An immediate bright yellow-orange color appeared; the mixture became homogenous (10–15 min) when the reaction was complete. Solvent was removed in vacuo to give **3** (1.133 g, 2.20 mmol, quantitative yield) as a yellow-orange powder. NMR data (C_6D_6): $^{31}\text{P}\{^1\text{H}\}$ NMR δ 59.1 (s); ^1H NMR δ 1.19 (*d*, $^3J_{\text{HH}}$ = 6.5 Hz, CH_3CH), 1.30 (d, $^3J_{\text{HH}}$ = 6.5 Hz, CH_3CH), 3.32 (sept d, $^3J_{\text{HH}}$ = 6.5 Hz, $^3J_{\text{HP}}$ = 13.0 Hz, $CH_3(CH)$, 5.87 (s, C_5H_5), 9.66 (d, $^2J_{\text{HP}}$ = 60.0 Hz, HC=N); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 24.42, 24.72, 25.17, 25.51 (s, CH_3CH), 49.05 (d, $^2J_{\text{CP}}$ = 9.0 Hz, CH_3CH), 111.27 (s, C_5H_5), 184.56 (d, $^1J_{\text{CP}}$ = 13.7 Hz, HC=N): IR ν(C=N) 1654 (w) cm^{-1}. Mass spectrum *m/e* 515. Anal. Calcd for $\text{C}_{23}\text{H}_{39}\text{ClN}_3\text{PZr}$: C, 53.61; H, 7.63. Found: C, 53.49; H, 7.61.

Preparation of $(i\text{-Pr}_2\text{N})_2\text{PC(H)=NPPh}_2$ (4). The following experiment is representative. A solution of chlorophosphine Ph_2PCl (0.126 g, 0.570 mmol) in 14 mL of THF was added dropwise to a freshly prepared solution of **3** (0.295 g, 0.570 mmol) in 8 mL of THF at −40 °C. The color changed immediately, resulting in a brown solution. At room temperature, solvent was removed in vacuo. The product was extracted from the residue with pentane (2 × 5 mL), and removal of the solvent gave **4** (0.177 g, 0.400 mmol, 70%) as a white solid. NMR data (C_6D_6): $^{31}\text{P}\{^1\text{H}\}$ NMR δ 56.5 (d, $^1J_{\text{PP}}$ = 26.2 Hz, PN), 60.6 (d, $^1J_{\text{PP}}$ = 26.2 Hz, PhP); ^1H NMR δ 1.16 (d, $^3J_{\text{HH}}$ = 6.5 Hz, CH_3CH), 3.32 (m, CH_3CH), 7.08, 7.48, 7.56 (m, aryl H), 8.62 (dd $^2J_{\text{HP}}$ = 56.7 Hz, $^3J_{\text{HP}}$ = 29.9 Hz, HC=N): $^{13}\text{C}\{^1\text{H}\}$ NMR δ 24.33, 24.64, 24.85, 25.18 (s, CH_3CH), 47.70 (d, $^2J_{\text{CP}}$ = 13.2 Hz, CH_3CH), 49.53 (d, $^2J_{\text{CP}}$ = 10.1 Hz, CH_3CH), 130.54–136.68 (m, aryl C), 178.21 (d, $^1J_{\text{CP}}$ = 24.7 Hz, $^2J_{\text{CP}}$ = 4.0 Hz, HC=N), 182.85 (d, $^2J_{\text{CP}}$ = 6.0 Hz, ipso C). Mass spectrum: *m/e* 443. Anal. Calcd for $\text{C}_{25}\text{H}_{39}\text{N}_3\text{P}_2$: C, 67.70; H, 8.86. Found: C, 67.59; H, 8.82.

Preparation of $(i\text{-Pr}_2\text{N})_2\text{PC(H)=NP(N-}i\text{-Pr}_2\text{)Cl}$ (5). In a procedure analogous to that given for **4**, **3** (0.286 g, 0.550 mmol), prepared in situ in 4 mL of THF, was treated with a THF solution (8 mL) of $i\text{-Pr}_2\text{NPCl}_2$ (0.112 g, 0.550 mmol) to give, after stirring 10 min at −20 °C, **5** (0.171 g, 0.440 mmol, 80%) as a beige oil. NMR data (C_6D_6): $^{31}\text{P}\{^1\text{H}\}$ NMR δ 59.1 (d, $^3J_{\text{PP}}$ = 21.8 Hz, PC), 135.7 (d, $^3J_{\text{PP}}$ = 21.8 Hz, PCl); ^1H NMR δ 1.10 (d, $^3J_{\text{HH}}$ = 6.3 Hz, CH_3CH), 1.17 (d, $^3J_{\text{HH}}$ = 6.3 Hz, CH_3CH), 3.28 (m, CH_3CH), 9.37 (d.d, $^2J_{\text{HP}}$ = 56.6 Hz, $_3J_{\text{HP}}$ = 35.0 Hz, HC=N); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 23.84, 24.17, 24.30, 24.49, 24.62, 24.82, 25.98, 26.15 (s, CH_3CH), 48.97 (d, $^2J_{\text{CP}}$ = 12.2 Hz, CH_3CH), 50.19 (d, $^2J_{\text{CP}}$ = 10.4 Hz, CH_3CH), 186.85 (d, $^1J_{\text{CP}}$ = 8.8 Hz, $^2J_{\text{CP}}$ = 5.1 Hz, HC=N). Mass spectrum: *m/e* 389. Anal. Calcd for $\text{C}_{19}\text{H}_{43}\text{N}_4\text{P}_2$: C, 58.59: H, 11.13. Found: C, 58.47; H, 11.02.

Preparation of $(i\text{-Pr}_2\text{N})_2\text{PC(H)=NP(N-}i\text{-Pr}_2\text{)}_2$ (6). Method A: In a procedure analogous to that given for **4**, **3** (0.465 g, 0.903 mmol), prepared in situ, was treated with a THF solution (10 mL) of $(i\text{-Pr}_2\text{N})_2\text{PCl}$ (0.241 g, 0.903 mmol) to give, after stirring 36 h at room temperature, **6** (0.331 g, 0.677 mmol, 75%) as a white solid. Method B: A Schlenk flask was charged with **3** (0.721 g, 1.400

(7) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *67*, 3895.
(8) King, R. B.; Sundaram, P. M. *J. Org. Chem.* **1984**, *49*, 1784.
(9) Jones, C. E.; Coskran, K. J. *Inorg. Chem.* **1971**, *10*, 1971.
(10) Higashi, J.; Eastman, A. D.; Parry, R. W. *Inorg. Chem.* **1982**, *21*, 716.

mmol), CH_2Cl_2 (20 mL), and a stir bar. The solution was cooled to −50 °C, then $Me_3SiOSO_2CF_3$ (0.270 mL, 1.400 mmol) was added. The reaction mixture was stirred for 1 h at −50 °C. Solvent was removed at room temperature in vacuo. The residue was extracted with pentane (2 × 5 mL). Removal of the solvent gave **6** (0.463 g, 1.190 mmol, 85%). NMR data (C_6D_6): $^{31}P\{^1H\}$ NMR δ 56.2 (d, $^3J_{PP}$ = 25.0 Hz, PC), 92.2 (d, $^3J_{PP}$ = 25.0 Hz, NP); ^1H NMR δ 1.08–1.34 (CH_3CH), 3.49 (m, CH_3CH), 9.14 (dd, $^2J_{HP}$ = 64.0 Hz, $^3J_{HP}$ = 30.0 Hz, HC=N); $^{13}C\{^1H\}$ NMR δ 24.45, 24.55, 24.63, 24.76, 24.87, 24.97, 25.02, 25.31 (s, CH_3CH), 46.37 (d, $^2J_{CP}$ = 12.0 Hz, CH_3CH), 49.48 (d, $^2J_{CP}$ = 10.0 Hz, CH_3CH), 178.60 (d, $^1J_{CP}$ = 23.0 Hz, HC=N). Mass spectrum: *m/e* 489. Anal. Calcd for $C_{25}H_{57}N_5P_2$: C, 61.32; H, 11.73. Found: C, 61.22; H, 11.61.

Preparation of $(i\text{-}Pr_2N)_2PC(H)=NB(N\text{-}i\text{-}Pr_2)_2$ (7). In a procedure analogous to that given for **4**, **3** prepared in situ in a toluene (40 mL) solution (**1** 1.26 g, 4.90 mmol: **2** 1.26 g, 4.89 mmol), was treated with a toluene (10 mL) solution of $(i\text{-}Pr_2N)_2BCl$ (1.21 g, 4.90 mmol) to give, after stirring 70 h, **7** (1.90 mg, 4.04 mmol, 83%) as a red-brown oil. NMR data (C_6D_6): $^{31}P\{^1H\}$ NMR δ 61.2 (s); ^{11}B NMR δ 31.8 (s); ^1H NMR δ 1.04–1.34 (CH_3CH), 3.43 (m, CH_3CH), 8.89 (d, $^2J_{HP}$ = 74.6 Hz, HC=N); $^{13}C\{^1H\}$ NMR δ 22.86, 23.45, 23.61, 23.97, 24.15, 24.55, 24.85, 25.18, 25.52 (s, CH_3CH), 46.20, 47.45 (s, CH_3CHNB), 47.72 (d, $^2J_{CP}$ = 11.6 Hz, CH_3CHNP), 49.93 (d, $^2J_{CP}$ = 9.6 Hz, CH_3CHNP), 170.58 (d, $^1J_{CP}$ = 6.0 Hz, HC=N); IR ν(C=N) 1657 (m) cm^{-1}. Mass spectrum: *m/e* 469. Anal. Calcd for $C_{19}H_{43}N_4P_2$: C, 58.59; H, 11.13. Found: C, 58.47; H, 11.02.

Preparation of $(i\text{-}Pr_2N)_2PC(H)=NBCl[N(SiMe_3)N(SiMe_3)_2]$ (8). In a procedure analogous to that given for **4**, **3** (0.487 g, 0.940 mmol), prepared in situ in toluene (4 mL), was treated with a toluene (8 mL) solution of $(Me_3Si)_2N(Me_3Si)NBCl_2$ (0.311 g, 0.940 mmol) to give, after stirring 30 min at −40 °C, **8** (0.440 g, 0.790 mmol, 85%) as a beige powder. NMR data (C_6D_6): $^{31}P\{^1H\}$ NMR δ 58.2 (s); ^{11}B NMR (C_6D_6) δ 31.4 (s); ^1H NMR (C_6D_6) δ 0.23 (s, $NSiCH_3$), 0.32 (s, $BNSiCH_3$), 0.97–1.23 (CH_3CH), 3.30 (m, CH_3CH), 9.20 (d, $^2J_{HP}$ = 49.9 Hz, HC=N); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 22.61, 23.06, 23.51, 24.03, 24.32, 24.61, 24.92, 25.14, 25.47 (s, CH_3CH), 50.07 (d, $^2J_{CP}$ = 12.4 Hz, CH_3CH), 50.12 (d, $^2J_{CP}$ = 10.0 Hz, $CH_3(CH)$, 184.34 (d, $^1J_{CP}$ = 8.8 Hz, HC=N). Mass spectrum: *m/e* 469. Anal. Calcd for $C_{19}H_{43}N_4P_2$: C, 58.59; H, 11.13. Found: C, 58.47; H, 11.02.

Registry No. **1**, 97135-49-4; **2**, 37342-97-5; **3**, 136044-16-1; **4**, 136044-18-3; **5**, 136044-19-4; **6**, 136044-20-7; **7**, 136044-21-8; **8**, 136044-22-9; **12**, 136044-23-0; **13**, 4791-48-4; **14**, 136044-17-2; Ph_2PCl, 1079-66-9; $(i\text{-}Pr_2N)PCl_2$, 921-26-6; $(i\text{-}Pr_2N)_2PCl$, 56183-63-2; $Me_3SiOSO_2CF_3$, 27607-77-8; $(i\text{-}Pr_2N)_2BCl$, 28049-80-1; $(Me_3Si)_2NN(SiMe_3)BCl_2$, 136044-24-1; Me_3SnCl, 1066-45-1.

Synthesis, NMR Studies, and Reactions with Tetracyanoethylene of (η^1-Allyl)(aryl)platinum(II) Complexes

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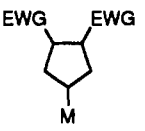
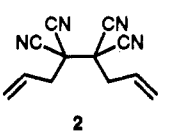
Received April 22, 1991

Summary: Some (η^1-allyl)(aryl)platinum(II) complexes of the type Pt(η^1-$CH_2CR{=}CH_2$)(Ar)(diphos) (R = H, Me; Ar = C_6F_5, $C_6H_3Cl_2$-2,5; diphos = $Ph_2PCH_2CH_2PPh_2$, (p-tol)$_2PCH_2CH_2P$(p-tol)$_2$) have been prepared from the corresponding η^3-allyl complexes Pt(η^3-CH_2CRCH_2)(Ar)(PPh$_3$) and diphosphines. ^1H NMR spectra of the 2,5-dichlorophenyl analogues were interpreted by occurrence of a restricted rotation of the aryl group about the Pt–C(Ar) bond. NOE experiments on the $CH_2CMe{=}CH_2$ derivatives suggested the occurrence of one dominant rotamer with regard to rotation about the C(α)—C(β) bond where the $CH_2{=}C(\beta)—C(\alpha)$ plane is nearly perpendicular to the Pt—C(α)—C(β) plane. Reactions of tetracyanoethylene with the η^1-$CH_2CH{=}CH_2$ analogues afforded formal [2 + 3] cycloadducts, whereas the reactions with the η^1-$CH_2CMe{=}CH_2$ analogues led to formation of linear adducts containing a $PtC(CN)_2C(CN)_2CH_2CMe{=}CH_2$ linkage.

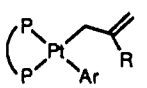
The η^1-allyl ligand bound to transition metals is known to be susceptible to the attack of electrophilic olefins, primarily resulting in the formation of [2 + 3] cycloadducts **1**.[1] Of the group 10 metal allyl analogues, platinum derivatives were shown to adopt the η^1-allyl form with the greatest ease,[2] and thus their reactions with the olefins were studied in more detail than for the palladium and nickel derivatives.[3-5] One class of the (η^1-allyl)platinum(II) complexes studied has the general formula Pt(allyl)(Cl)(PR$_3$)$_2$, in which the reactive η^1-allyl form Pt(η^1-allyl)(Cl)(PR$_3$)$_2$ exists only as an equilibrium mixture with the cationic η^3-allyl form [Pt(η^3-allyl)(PR$_3$)$_2$]$^+$Cl$^-$, even



1



2



3a: R = H, Ar = C_6F_5, P⌒P = dppe
b: R = H, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dppe
c: R = H, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dtpe
d: R = Me, Ar = C_6F_5, P⌒P = dppe
e: R = Me, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dppe
f: R = Me, Ar = $C_6H_3Cl_2$-2,5, P⌒P = dtpe

dppe = $Ph_2PCH_2CH_2PPh_2$; dtpe = (p-tol)$_2PCH_2CH_2P$(p-tol)$_2$

(1) (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) Wojcicki, A. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 100. (c) Dodd, D.; Johnson, M. D.; Steeples, I. P.; McKenzie, E. D. *J. Am. Chem. Soc.* **1976**, *98*, 6399. (d) Wright, M. E.; Hoover, J. F.; Nelson, G. O.; Scott, C. P.; Glass, R. S. *J. Org. Chem.* **1984**, *49*, 3059. (e) Glass, R. S.; McConnell, W. W. *Organometallics* **1984**, *3*, 1630.

(2) (a) Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *16*, 1737. (b) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Kruger, C. *J. Organomet. Chem.* **1980**, *191*, 449. (c) Kurosawa, H. *J. Organomet. Chem.* **1987**, *334*, 243.

(3) (a) Calligaris, M.; Carturan, G.; Nardin, G.; Scrivanti, A.; Wojcicki, A. *Organometallics* **1983**, *2*, 865. (b) Bertani, R.; Carturan, G.; Scrivanti, A.; Wojcicki, A. *Organometallics* **1985**, *4*, 2139. (c) Hu, Y. R.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1987**, *6*, 1561.

(4) Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002.

(5) Benn, R.; Gabor, G.; Jolly, P. W.; Mynott, R.; Raspel, B. *J. Organomet. Chem.* **1985**, *296*, 443.

0276-7333/91/2310-3941$02.50/0