erated zirconocene–benzyne species, followed by treatment of the intermediate metallacycles with an appropriate electrophile, the net syn 1,2-difunctionalization of the cyclic olefin can be effected. The work described represents some of the first examples of such cis carbofunctionalizations. We are currently probing the generality of this reaction strategy in order to extend this methodology to the synthesis of other carbocyclic and heterocyclic systems.

Acknowledgment. We thank the National Institutes of Health for financial support, the ICFES-BID-UIS for a 3-month fellowship (A.G.), and Drs. William Davis and Richard Fisher for the X-ray crystal structure.

Supplementary Material Available: Experimental details concerning the preparations and spectroscopic and analytical characterizations of the compounds, experimental details for the crystallographic analysis of 5, an ORTEP diagram, and lists of atom positions, thermal parameters, and bond lengths and angles (16 pages). Ordering information is given on any current masthead page.

Application of Phosphine and Arsine–Phosphoranimine Backbones to the Formation of Early–Late-Transition-Metal Bimetallics. Synthesis and Characterization of New Titanium–Palladium Frameworks: $(\eta^5\text{-}C_5H_5)Cl_2Ti\overline{N{=}PPh_2(CH_2)_xEPh_2P}dCl_2$ (x = 1, E = P; x = 2, E = As)

Kattesh V. Katti and Ronald G. Cavell*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received July 2, 1990

Summary: Titanium–palladium bimetallics of the form $CpCl_2Ti{-}\overline{N{=}PPh_2(CH_2)_xPPh_2P}dCl_2$ can be prepared from the phosphine (or arsine) phosphoranimines $Ph_2P(CH_2)_xEPh_2{=}NSiMe_3$ (E = P, x = 1; E = As, x = 2) by either of two routes: (a) metathetical replacement of $SiMe_3$ by $CpTiCl_2$ followed by complexation of $PdCl_2$ or (b) complexation of the phosphoranimine ligand with $PdCl_2$ followed by reaction of the complex with $CpTiCl_3$ to form the bimetallic and Me_3SiCl.

There are many reasons for seeking means of constructing transition-metal heterobimetallic complexes connecting the "early" and "late" metals. These systems may provide models for the complex phenomena of "strong metal–support interactions", which are apparent in heterogeneous catalysts.[1] In addition, bimetallics may yield useful new homogeneous catalysts providing directed synthesis of specific organics.[2]

Although there has been considerable interest and significant achievements[3] in constructing such systems in recent years, a major barrier to success is presented by the general difficulty of developing compounds that can simultaneously and effectively bind both the early and the late transition metals, a combination which necessarily presents widely differing chemical reaction character.

Table I. Phosphorus-31 NMR[a] Spectroscopic Data for the Phosphoranimine–Phosphine and –Arsine Ligands and Their Mono- and Bimetallic Complexes

compd	$\delta_{P^{III}}$	$\delta_{P^{V}}$	$^2J_{PP}$, Hz
$Me_3SiN{=}PPh_2CH_2PPh_2$ (1)[b]	−28.2	−1.4	57.7
$(\eta^5\text{-}C_5H_5)Cl_2TiN{=}PPh_2CH_2PPh_2$ (3)[b]	−29.0	38.6	59.7
$Me_3Si\overline{N{=}PPh_2CH_2PPh_2P}dCl_2$ (5)[c]	16.6	34.8	26.2
$(\eta^5\text{-}C_5H_5)Cl_2Ti\overline{N{=}PPh_2CH_2PPh_2P}dCl_2$ (7)	16.2	33.4	8.0
$H\overline{N{=}PPh_2CH_2PPh_2P}dCl_2$ (9)[c]	25.2	53.8	29.9
$Me_3SiN{=}PPh_2CH_2CH_2AsPh_2$ (2)[d]		1.8	
$(\eta^5\text{-}C_5H_5)Cl_2TiN{=}PPh_2CH_2CH_2AsPh_2$ (4)		40.1	
$Me_3Si\overline{N{=}PPh_2CH_2CH_2AsPh_2P}dCl_2$ (6)[c]		32.8	
$(\eta^5\text{-}C_5H_5)Cl_2Ti\overline{N{=}PPh_2(CH_2)_2AsPh_2P}dCl_2$ (8)		43.0	

[a] All spectra in $CDCl_3$; in ppm vs 85% H_3PO_4. [b] Data from ref 7. [c] Data from ref 8. [d] Data from ref 9.

There are, of course, many conventional heterodifunctional (and polyfunctional) ligand systems available, but it seemed desirable to us to also attempt to form one metal–element σ bond for enhanced stability. Typical examples of such systems are the functionalized phosphine derivatives Ph_2PCH_2O–[4] and $Ph_2PCH_2CH_2S$–[5] of the early metals Ti and Zr containing oxygen or sulfur to metal σ bonds. The free phosphine center in these compounds can then be used to coordinate late metals such as Pd and Rh to form early–late bimetallics. Extensive examples are given in ref 3.

We have synthesized a variety of new bifunctional silylimino–phosphorus and –arsenic ligands[6-9] (1, 2), which also show considerable promise as versatile backbones for heterobimetallics of the transition metals and in addition

---

(1) (a) Imelik, B., Naccache, C., Coudurier, G., Praliaud, H., Meriaudeau, P., Galizot, P., Martin, G. A., Verdin, J. C., Eds. *Metal-Support and Metal-Additive Effects in Catalysis*; Elsevier: New York, 1982. (b) Baker, R. T. K., Tanster, S. J., Dumesic, J. A., Eds. *Strong Metal-Support Interactions*; American Chemical Society: Washington, DC, 1986. (c) Stevenson, S.; Baker, R. T. K.; Dumesic, J. A. *Metal Support Interactions*; Van Nostrand: New York, 1988.

(2) See for example: (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 6, pp 763–877. (b) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665. (c) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504. (d) Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218. (e) Casey, C. P.; Palermo, R. E.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 4597. (f) Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *108*, 6069. (g) Wark, T. A.; Stephan, D. W. *Inorg. Chem.* **1984**, *26*, 363 and references therein. (h) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167 and references therein. (i) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4853. (j) Jacobsen, E. N.; Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3706. (k) White, G. S.; Stephan, D. W. *Organometallics* **1988**, *7*, 903. (l) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (m) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319. (n) Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8.

(3) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 4107.

(4) Ferguson, G. S.; Wolczanski, P. T. *Organometallics* **1985**, *4*, 1601. Ferguson, G. S.; Wolczanski, P. T.; Parkanyi, L.; Zonnevylle, M. C. *Organometallics* **1988**, *7*, 1967.

(5) White, G. S.; Stephan, D. W. *Inorg. Chem.* **1985**, *24*, 1499.

(6) Katti, K. V.; Cavell, R. G. *Organometallics* **1988**, *7*, 2236.

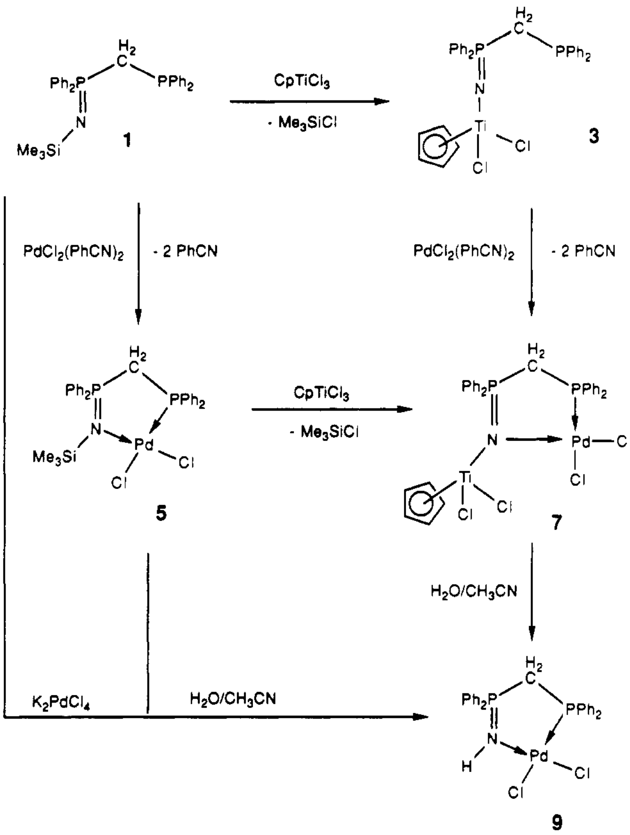
(7) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 413.

(8) Katti, K. V.; Batchelor, R. J.; Einstein, F. W.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 808.

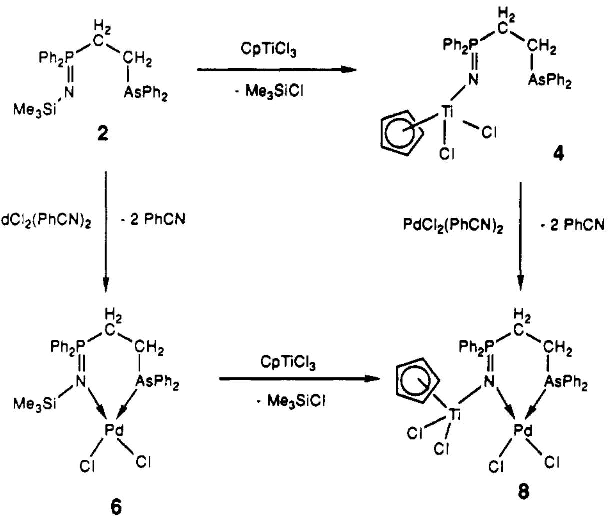
(9) Katti, K. V.; Cavell, R. G. *Organometallics* **1989**, *8*, 2147.

0276-7333/91/2310-0539$02.50/0

Scheme I



Scheme II



provide an easily accessed route to the formation of the metal–N σ bond. The partially metalated derivatives 3[7] and 4, readily derived from 1 and 2 via elimination of Me_3SiCl, provide examples in which an early transition metal in a high oxidation state (e.g., Ti(IV)) is chemically bound via a M–N σ bond to the ligand system. There remains in these compounds two available coordinative functionalities; a hard N and a soft P(III) or As(III) base. The soft base in 3 and 4 should combine readily with late transition metals in low oxidation states to form heterobimetallics. Herein we report new and versatile synthetic strategies to two Pd(II)–Ti(IV) compounds that demonstrate this possibility. The versatility of the system is further demonstrated by our ability to reach each of the final products by two synthetic routes; we can first form the early-metal compound and then introduce the late-metal moiety or vice versa. The processes are depicted in Schemes I and II.

The reaction of 3 with $PdCl_2(PhCN)_2$ or of 5[10] with $CpTiCl_3$ proceeded smoothly in CH_2Cl_2 at room temperature to form 7, the first example of a Ti(IV)–Pd(II) heterobimetallic compound built on a phosphoranimine–phosphine skeleton, in almost quantitative yields.[11] The compound is a relatively air-stable crystalline solid that is monomeric in solution. The ^{31}P NMR spectrum of 7 and the comparison of the data with those of the precursors 1, 3, and 5 (Table I) confirms the formulation and reveals some notable features that appear in these bimetallic systems. First, there is a significant decrease of the $^2J_{PP}$ value in the series 3 (59.7 Hz),[7] 5 (26.2 Hz),[8] and 7 (8.0 Hz), which may be a consequence of increased electron withdrawal from the P–C–P unit by the bimetallic Ti–N–Pd part of the skeleton in 7. The incorporation of the metal (Pd) center in both 5 and 7 results in a considerable deshielding of the P(III) center to which the Pd is bound (from −28.95 ppm in 3 to 16.16 ppm in 7 and 16.94 ppm in 5). The similarity of P(III) chemical shifts in both 7 and 5 can perhaps be rationalized by the fact that both are bound to Pd(II). The differences in the chemical shifts of the phosphoraniminato phosphorus ($-N{=}PPh_2$) unit in 3 (38.64 ppm), 5 (34.81 ppm), and 7 (33.40 ppm) are not significant, although it is clear that introduction of Ti in place of Si (3 vs 1) causes a substantial deshielding of the P(V) center.

Aqueous acetonitrile hydrolyzes the Ti–N bond in 7 to produce the previously characterized metallacycle 9[8] almost quantitatively (Scheme I) plus an insoluble titanium compound similar to that arising from the hydrolysis of $CpTiCl_3$ itself. Additional reactivity studies are in progress.

In very parallel chemistry, reaction of $CpTiCl_3$ with $Me_3SiN{=}PPh_2CH_2CH_2AsPh_2$ (2) in dichloromethane afforded 4 in good yields (Scheme II). Compound 4, which is also a relatively air-stable crystalline solid and which is also monomeric in solution, represents the first example of a transition-metal-functionalized phosphorus-containing arsine.[12] Subsequent reaction of 4 with $PdCl_2(PhCN)_2$ gave good yields of the new Ti(IV)–Pd(II) heterobimetallic compound 8.[13] Spectroscopic data are given in Table I.

---

[10] 5 was prepared almost quantitatively by the reaction of equimolar quantities of 1 and $PdCl_2(PhCN)_2$ in dichloromethane at room temperature. Complete details are given in ref 8.

[11] (a) In a typical reaction a solution of $CpTiCl_3$ (0.10 g; 0.46 mmol) in dichloromethane (25 mL) was added dropwise with stirring at 0 °C to a dichloromethane (25 mL) solution of 5 (0.30 g; 0.46 mmol). After the mixture was stirred for 10 h, the solvent was removed in vacuo to give the analytically pure brown microcrystalline solid 7 (yield 92%; mp 210 °C dec). Anal. Calcd for $C_{30}H_{27}Cl_4NP_2PdTi$: C, 47.40; H, 3.55; N, 1.84; Cl, 18.67. Found: C, 47.52; H, 3.61; N, 1.81; Cl, 18.70. ^1H NMR ($CDCl_3$): phenyl rings δ 7.30, 7.56, 7.80 (m, 20 H); PCH_2P methylene δ 3.95 (t, 2 H, $^2J_{PH}$ = 13.10 Hz); cyclopentadienyl ring δ 6.70 (s, 5 H). (b) The reaction of $PdCl_2(PhCN)_2$ with 3 was carried out under experimental conditions similar to those described above (yield of 7 87%). The physical constants, analytical data, and spectroscopic data for this product were identical with those listed above.

[12] 4 was synthesized by dropwise addition of a solution of $CpTiCl_3$ (0.72 g; 3.31 mmol) in dichloromethane (50 mL) to a solution of 2 (1.75 g; 3.31 mmol) also in dichloromethane (50 mL) at 25 °C. After the mixture was stirred for 4 h, the titanium compound 4 was obtained as a bright yellow microcrystalline solid upon removal of the solvent in vacuo. Further purification of 4 was achieved by washing the crude product with diethyl ether at 0 °C (20 mL) (yield of 4 1.95 g, 92%; mp 148 °C dec). Anal. Calcd for $C_{31}H_{29}Cl_2NAsPTi$: C, 58.22; H, 4.53; N, 2.19; Cl, 11.09. Found: C, 58.17; H, 4.47; N, 2.18; Cl, 11.12. ^1H NMR ($CDCl_3$): phenyl rings δ 7.35, 7.65, 7.85 (m, 20 H); $AsCH_2CH_2P$ δ 2.30 (m, 2 H), 2.70 (m, 2 H); cyclopentadienyl ring δ 6.50 (s, 5 H).

The bimetallic compound 8 is also stable in strongly coordinating solvents such as CH_3CN or THF but does react with water and protonic solvents.

Parallel to the chemistry demonstrated for the phosphoranimines, an alternate route to the new arsenic-based Ti(IV)–Pd(II) bimetallic 8 was provided by the reaction of the Pd(II) complex 6, readily formed from 2 and $PdCl_2(PhCN)_2$, with $CpTiCl_3$ (Scheme II).

The new methodology for formation of early–late-transition-metal bimetallics (Schemes I and II) promises to provide a versatile route, because the precursors of types 5 and 6 are readily accessible for a variety of late (such as Rh(I), Ir(I), or Pd(II)) metals and compounds such as 3 and 4 are readily synthesized for early (such as W(VI), Zr(IV), V(V)) transition metals.[10] Further applications of the sequences described herein are presently under investigation.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

---

(13) (a) The reaction of $PdCl_2(PhCN)_2$ with 4 to obtain 8 was carried out under experimental conditions similar to those described above for the preparation of 7[11] (yield of 8 90%; mp 190 °C dec). Anal. Calcd for $C_{31}H_{29}Cl_4NAsPPdTi$: C, 41.83; H, 3.26; N, 1.57; Cl, 15.94. Found: C, 41.78; H, 3.28; N, 1.55; Cl, 15.92. ^1H NMR ($CDCl_3$): phenyl rings δ 7.40, 7.67, 7.87 (m, 20 H); $AsCH_2CH_2P$ δ 2.60 (m, 2 H), 3.20 (m, 2 H); cyclopentadienyl ring δ 6.65 (s, 5 H). (b) The reaction of $CpTiCl_3$ with 6 (prepared as described in ref 8) was carried out under experimental conditions similar to those described above for the transformation of 5 to 7 (yield 85%). The physical constants, analytical data, and spectroscopic data for 8 prepared via this route were identical with those listed above.

Direct Observation of the Low-Valent Hydrazido Complex $(CO)_5W{=}NNMe_2$, a Nitrene Analogue of the Heteroatom-Stabilized Fischer Carbenes

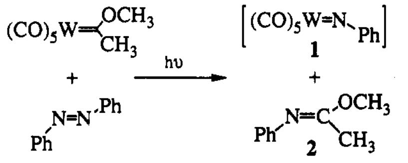
Hanadi F. Sleiman, Bruce A. Arndtsen, and Lisa McElwee-White*

Department of Chemistry, Stanford University, Stanford, California 94305

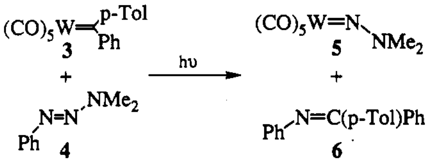
Received December 18, 1990

Summary: The low-valent hydrazido (or heteroatom-stabilized nitrene) complex $(CO)_5W{=}NNMe_2$ (**5**) was synthesized via photochemical metathesis of the triazene $PhN{=}NNMe_2$ (**4**) with $(CO)_5W{=}C(p\text{-Tol})Ph$ (**3**). Assignment of **5** as a bent terminal hydrazido complex was made on the basis of its multinuclear NMR and IR spectra.

We recently reported the generation of the low-valent tungsten nitrene $(CO)_5W{=}NPh$ (1) by reaction of $(CO)_5W{=}C(OMe)Me$ with photochemically generated *cis*-azobenzene (eq 1). Complex 1 was not directly observed but, rather, was identified by its trapping and decomposition products.[1,2] Although 1 and its chromium congener have been invoked as intermediates in the reactions of Fischer carbenes with azo compounds and nitroso compounds,[3] these species have not yet been directly observed. We now report the generation and direct observation of the low-valent hydrazido (or heteroatom-stabilized nitrene) complex $(CO)_5W{=}NNMe_2$ (5) from the photochemical metathesis between $(CO)_5W{=}C(p\text{-Tol})Ph$ (3) and the triazene $PhN{=}NNMe_2$ (4) (eq 2). Although 5 could not be isolated, it is persistent for several hours in solution at room temperature and has been characterized through IR and multinuclear NMR spectroscopy.



(1)



(2)

Metal hydrazido complexes are common in the literature, but the reported examples are almost exclusively confined to high-valent metals with two or less d electrons.[4] In general, the lack of electron density around the metal causes the hydrazido ligands to adopt the linear (or nearly linear) geometry required for donation of 4e, so that strongly bent terminal hydrazido complexes have remained extremely rare.[5] The low-valent hydrazido complex 5 is electronically quite different, in that 4e donation would result in a 20e complex and bending of the hydrazido ligand is expected.[6] Given that 5 and the related nitrene (or imido) complex 1 are isoelectronic with Fischer carbenes, insight into their properties is perhaps better gained by comparing 5 and 1 to the carbene complexes.

Fischer carbenes of the type $(CO)_5M{=}CRR'$ (R, R′ = H, alkyl, aryl) are highly reactive, highly electrophilic species, while their heteroatom-substituted counterparts

---

(1) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701.

(2) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007–8009.

(3) (a) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263–1267. (b) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665–3668. (c) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83–101.

(4) Recent reviews on hydrazido complexes include (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Hidai, M. In *Molybdenum Enzymes*; Wiley-Interscience: New York, 1985; pp 285–341. (c) Chatt, J.; da Camara Pina, L. M.; Richards, R. L., Eds. *New Trends in the Chemistry of Nitrogen Fixation*; Academic Press: London, 1980.

(5) For examples of structurally characterized bent hydrazido complexes see: (a) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578–2585. (b) Einstein, F. W. B.; Jones, T.; Hanlan, A. J. L.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2585–2589.

(6) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. Submitted for publication.

0276-7333/91/2310-0541$02.50/0