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Highly Bulky and Electron-Rich Terminal Ruthenium Phosphido Complexes: New Donor Ligands for Palladium-Catalyzed Suzuki Cross-Couplings

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Secondary phosphine complexes of the formula $[(\eta^5\text{-}C_5H_5)Ru(L)_2(PHR_2)]^+ \, BAr_F^-$ are prepared from cationic ruthenium N_2 complexes and PHR_2 ($R = Ph$ (**a**), *t*-Bu (**b**), Cy (**c**)). Additions of *t*-BuOK or $NaN(SiMe_3)_2$ give the phosphido complexes $(\eta^5\text{-}C_5H_5)Ru(L)_2(PR_2)$ ($(L)_2 = (PEt_3)_2$ (**5a**–**c**), depe (**6a**,**b**)) in high NMR yields. These rapidly oxidize in air to give isolable $RuP(=O)R_2$ species. Complex **5a** is more basic than the rhenium analogue $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2)$, and **6b** is more basic than P-*t*-Bu_3. Complexes **5a**–**c** and **6b** are effective ligands for palladium-catalyzed Suzuki reactions. The catalyst from **6b** is nearly as reactive as that from the benchmark ligand P-*t*-Bu_3.

Over the past few years, numerous new types of phosphorus donors have been evaluated as ligands in metal-catalyzed organic transformations. Improved performance characteristics are often found with species that are bulkier and/or more electron-rich.[1] In this context, we have been interested in coordinatively saturated phosphido complexes of the type L_nMPR_2: as ligands for metal-catalyzed reactions.[2,3] Our efforts to date have focused on rhenium(I) systems of the formula $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(PR_2)$, in which the pyramidal PR_2 moiety is much more congested and nucleophilic than in organic analogues PR_3.[2,4] However, we sought to develop new series of phosphido complexes that would be still more electron-rich. Our attention was drawn to ruthenium(II) species of the type $(\eta^5\text{-}C_5R_5)Ru(PR_3)_2(X)$, in which the strongly π accepting NO ligand of the rhenium has been eliminated. Many such adducts are known where X is a halide, alkoxide, or thiolate ligand, or $(PR_3)_2$ constitutes a chiral diphosphine ligand.[5,6] However, to our knowledge no phosphido complexes are yet described.[7,8] In this communication, we report that such species are (1) easily generated, (2) among the most electron rich trivalent phosphorus compounds known, and (3) highly effective ligands for palladium-catalyzed Suzuki coupling reactions.

In view of the congested nature of the target compounds, building blocks with good leaving groups were sought. Our attention was drawn to the recently reported and easily prepared bis(tertiary phosphine) dinitrogen complexes **1** and **2** shown in Scheme 1.[9] These were treated with the secondary phosphines $PHPh_2$ (**a**), PH-*t*-Bu_2 (**b**), and $PHCy_2$ (**c**) under homogeneous conditions in C_6H_5F at room temperature. As shown in Scheme 1, workups gave the new secondary phosphine complexes $[(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PHR_2)]^+ \, BAr_F^-$ (**3a**−**c**) and $[(\eta^5\text{-}C_5H_5)Ru(depe)(PHR_2)]^+ \, BAr_F^-$ (**4a**,**b**)[10] in

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(1) The following references treat the Suzuki reaction, but many additional examples are cited therein: (a) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550. (b) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (c) Zapf, A.; Ehrentraut, A.; Beller, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4153; *Angew. Chem.* **2000**, *112*, 4315. (d) Clarke, M. L.; Cole-Hamilton, D. J.; Woolins, J. D. *J. Chem. Soc., Dalton Trans.* **2001**, 2721. (e) Li, G. Y. *J. Org. Chem.* **2002**, *67*, 3643. (f) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553.

(2) (a) Kromm, K.; Zwick, B. D.; Meyer, O.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2001**, *7*, 2015. (b) Kromm, K.; Hampel, F.; Gladysz, J. A. *Helv. Chim. Acta* **2002**, *85*, 1778. (c) Eichenseher, S.; Kromm, K.; Delacroix, O.; Gladysz, J. A. *Chem. Commun.* **2002**, 1046. (d) Kromm, K.; Osburn, P. L.; Gladysz, J. A. *Organometallics* **2002**, *21*, 4275.

(3) This is part of a general effort involving donor ligands that incorporate some type of "spectator metal", outside of metallocenes such as ferrocene. See: Delacroix, O.; Gladysz, J. A. *Chem. Commun.*, in press (feature article).

(4) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427.

(5) (a) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 4, pp 775−796. (b) Bennett, M. A.; Khan, K.; Wenger, E. In *Comprehensive Organometallic Chemistry II*, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 7, pp 476−527. (c) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761.

(6) Bell, P. T.; Cagle, P. C.; Vichard, D.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4695.

(7) For ruthenium phosphido complexes of the formula $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(PRX)$, see: (a) Stasunik, A.; Wilson, D. R.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C18. (b) Weber, L.; Reizig, K.; Boese, R. *Organometallics* **1985**, *4*, 2097.

(8) For ruthenium phosphido complexes of the formula $Ru(CO)_2(PPh_3)_2(Cl)(PRH)$, see: (a) Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1986**, *5*, 1612. (b) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Taylor, M. J. *J. Organomet. Chem.* **1988**, *348*, 385.

(9) Aneetha, H.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 628.

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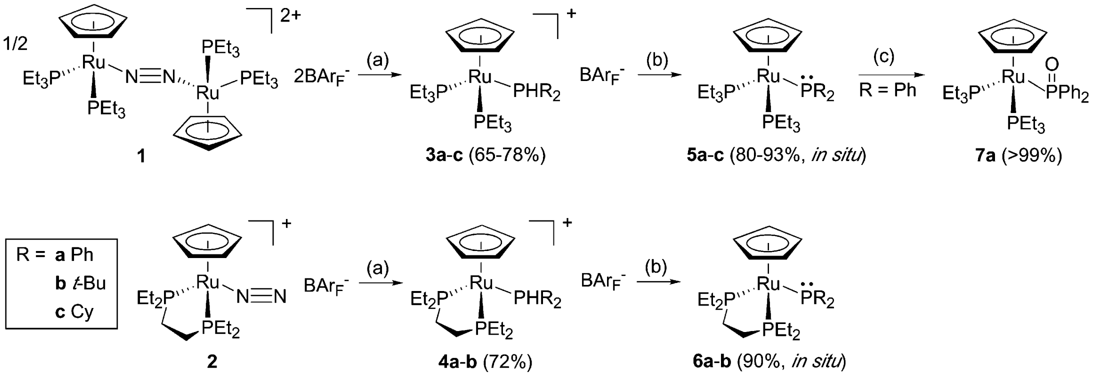
Scheme 1. Syntheses and Reactions of New Ruthenium Complexes[a]



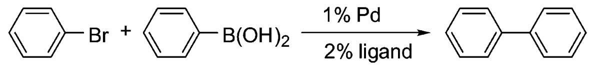
[a] Conditions: (a) PHR_2, C_6H_5F; (b) *t*-BuOK (**3a**, **4a**) or $NaN(SiMe_3)_2$ (**3b**,**c**, **4b**); (c) air.

65−78% yields as air-stable powders. Each was characterized by microanalysis and NMR, as summarized in the Supporting Information. The ^{31}P NMR spectra exhibited typical AX_2 patterns arising from the secondary and two equivalent tertiary phosphine ligands ($^2J(PP) = 31.3-42.0$ Hz). The ^1H NMR spectra showed diagnostic doublets of triplets for the PH signals ($^1J(HP)/^3J(HP) = 352.9/4.0$ (**3a**), 350.5/5.2 (**4a**), 327.7/4.0 (**3c**), 318.9/2.0 (**4b**), 316.5/2.4 (**3b**) Hz).

Deprotonations of the secondary phosphine complexes were attempted in NMR tubes.[11] Yellow acetone-d_6 solutions of **3a** and **4a** were treated with 1.0−1.1 equiv of *t*-BuOK. The solutions turned bright orange, and ^1H and ^{31}P NMR spectra (Supporting Information)[12] were consistent with the formation of target phosphido complexes $(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(PPh_2)$ (**5a**; 93% conversion) and $(\eta^5\text{-}C_5H_5)Ru(depe)(PPh_2)$ (**6a**; 90% conversion). Under analogous conditions, **3b**,**c** and **4b** did not react. However, when the much stronger base $NaN(SiMe_3)_2$ was added to THF-d_8 solutions (1.1−1.5 equiv), high conversions to phosphido complexes **5b** (80%), **5c** (95%), and **6b** (90%) were observed.[11] Attempts to isolate **5a**−**c** and **6a**,**b** always gave some of the corresponding phosphine oxide, and traces were always detected in the NMR tubes. When air was deliberately added, conversions were complete within seconds, much faster than for the analogous rhenium complexes. In the case of **5a**, the oxide $(\eta^5\text{-}C_5H_5)Ru(PEt_3)_2(P(=O)Ph_2)$ (**7a**) was isolated in >99% yield.

Hence, by analogy to protocols developed for other oxidation-sensitive electron-rich phosphines used in metal-catalyzed reactions,[2c,13] **5a**−**c** and **6a**,**b** were "stored" as the precursors **3a**−**c** and **4a**,**b**, and generated by in situ deprotonation. They were first evaluated in the palladium-catalyzed Suzuki reaction of bromobenzene and phenylboronic acid, for which we reported data with the rhenium complexes $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(PR_2)$ earlier. The conditions summarized in entries 1−4 of Table 1 ($Pd(OAc)_2/K_3PO_4$/toluene, 80 °C) share certain features with those used by Buchwald and Fu,[1a,b] and **5a**−**c** and **6b** were generated with 2.0 equiv of the bases described above (complete conversions).[14] Phenyl bromide was consumed as depicted in Figure 1. The catalysts derived from P-*t*-Bu_2 and PCy_2 complexes **5b**,**c** were distinctly more reactive than that derived from PPh_2 complex **5a** (less bulky and electron-rich ligand). The depe-substituted P-*t*-Bu_2 complex **6b** gave a still more active catalyst. The palladium source $Pd_2(dba)_3$[10c] did not give improved results, and in the absence of a phosphido complex rates were much slower and only partial conversion could be effected.

Table 1. Suzuki Coupling Reactions



entry[a]	ligand/Pd	conversion[b] (PhBr) (%)	yield[b] (Ph_2) (%)	time (h)
1	**6b**/$Pd(OAc)_2$	100	95	1
2	**5c**/$Pd(OAc)_2$	100	97	2
3	**5b**/$Pd(OAc)_2$	100	96	2
4	**5a**/$Pd(OAc)_2$	96	94	32
5	**5a**/$Pd_2(dba)_3$	88	81	32
6	none/$Pd(OAc)_2$	63	59	48

[a] General reaction conditions: bromobenzene (0.432−0.526 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_3PO_4 (2.0 equiv), $Pd(OAc)_2$ (1.0 mol %) or $Pd_2(dba)_3$ (0.5 mol % = 1.0 mol % Pd), 2 mol % ligand (deprotonated in situ), toluene, 80 °C. [b] Conversion and yield determined by GC (average of at least two runs), based on tridecane standard.

The activity of the catalyst system derived from **6b** is very slightly lower than that of the related rhenium complex $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(P\text{-}t\text{-}Bu_2)$ reported earlier,[2c] but higher than those of $RePPh_2$ and $RePMe_2$ analogues. In order to verify that the ruthenium complexes are more electron rich, an NMR tube was charged with a 1:1 mixture of **3a** and the corresponding rhenium secondary phosphine complex $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(PHPh_2)]^+\ TfO^-$,[2a,4] and 1.0 equiv of *t*-BuOK in acetone-d_6 was added. NMR spectra showed

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(10) Abbreviations: (a) $BAr_F^- = B[3,5\text{-}(C_6H_3(CF_3)_2)]_4^-$; (b) depe = $Et_2PCH_2CH_2PEt_2$; (c) dba = dibenzylidene acetone.

(11) For the simultaneous deprotonation and complexation of the ruthenium secondary phosphine complex $[(\eta^5\text{-}C_5H_5)Ru(CO)_2(PPh_2H)]^+\ BF_4^-$ by a platinum compound, see: Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, M. V. R. *Organometallics* **1990**, *9*, 387.

(12) The cyclopentadienyl ^1H NMR signals of **5a**−**c** and **6a**,**b** were 0.5−0.8 ppm upfield from those of **3a**−**c** and **4a**,**b**, and the *J*(P,P) values decreased markedly. When the samples were stored for 24 h, significant reprotonation to **5a**−**c** and **6a**,**b** occurred, perhaps due to slow-reacting hydroxylic moieties associated with the glass.

(13) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295.

(14) A detailed procedure is provided in the Supporting Information. A ^{31}P NMR experiment shows that the phosphido complex **5a** reacts upon addition of $Pd(OAc)_2$, and that subsequent addition of phenylboronic acid does not give detectable amounts of the protonation product **3a**.

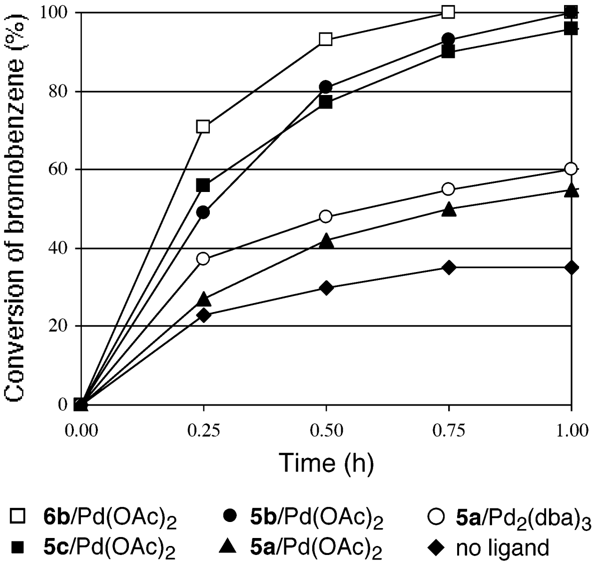

Figure 1. Consumption of bromobenzene under the conditions of Table 1.

the complete conversion of the latter to (η^5-C_5R_5)Re(NO)(PPh$_3$)(PPh$_2$), and no reaction of **3a**. Hence, **5a** has a much higher Brønsted basicity than its rhenium counterpart, and catalytic activity is not directly correlated to this property. Similarly, the best RuP-*t*-Bu$_2$ and ReP-*t*-Bu$_2$ catalyst systems remain slightly less active than that derived from P-*t*-Bu$_3$,[2c] which is one of the best ligands for the Suzuki reaction.[1b] An NMR tube was therefore charged with a 1:1 mixture of **4b** and [HP-*t*-Bu$_3$]$^+$ BF$_4^-$,[13] and 1.0 equiv of NaN(SiMe$_3$)$_2$ in THF-d_8 was added. NMR spectra showed complete deprotonation of the latter, and no reaction of **4b**. Hence, **6b** has a much higher Brønsted basicity than P-*t*-Bu$_3$.[15]

In summary, this study has significantly expanded the scant literature on ruthenium phosphido complexes.[7,8,11] Although no quantitative acid/base measurements were conducted, the lack of reactivity of **3b**,**c** and **4b** toward *t*-BuOK and P-*t*-Bu$_3$ indicates that the title compounds are among the most basic trivalent phosphorus compounds.[16] Accordingly, they should be excellent synthetic building blocks. The title compounds are also very effective ligands for metal-catalyzed reactions, and they approach the reactivities of the best organophosphines in palladium-catalyzed Suzuki reactions. These promising lead results are easily amenable to further optimization and extendable to chiral, nonracemic ruthenium systems. In the former context, we are currently attempting to more efficiently enter the catalytic cycle with preformed MPR$_2$Pd systems, such that the steric and electronic effects of these novel metal-containing phosphorus donor ligands upon reactivity can be more exactly evaluated.

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Supporting Information Available: Experimental procedures and NMR data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) There is furthermore, within homologous series of compounds, a correlation of ^1J(HP) values of protonated phosphines and basicity. The couplings of **3b** and **4b** are much lower than that of [HP-*t*-Bu$_3$]$^+$ BF$_4^-$ (318.9−316.5 vs 436 Hz), consistent with greater p character in the phosphorus bonding orbital and enhanced basicity. See: Hudson, H. R. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1990; Vol. 1, Chapter 12.

(16) Recent lead references: (a) Alder, R. W.; Butts, C. P.; Orpen, A. G.; Read, D.; Oliva, J. M. *J. Chem. Soc., Perkin Trans. 2* **2001**, 282. (b) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155. (c) Kisanga, P. B.; Verkade, J. G.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 5431. Note that in this case the conjugate acid is a hypervalent phosphorus compound.