

Preliminary Communication

Thermally Stable Arylpalladium Diamine Complexes as Versatile Precursors in Organopalladium Chemistry; Synthesis and X-Ray Molecular Structure of PdIPh(tmeda) and its Conversion to PdMePh(tmeda) {tmeda = Me₂N(CH₂)₂NMe₂}

Wim de Graaf,^a John van Wegen,^a Jaap Boersma,^{a*} Anthony L. Spek,^b and Gerard van Koten^a

^a Department of Metal-Mediated Synthesis, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands.

^b Department of Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands.

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Abstract: The new complex PdIPh(tmeda) (**1**) {tmeda = Me₂N(CH₂)₂NMe₂} was prepared by oxidative addition of iodobenzene to {bis(dibenzylideneacetone)}palladium(0) in the presence of tmeda and has been characterized by NMR spectroscopy and X-ray crystallography. Treatment with MeLi affords the remarkably stable mixed diorgano species PdMePh(tmeda) (**2**). Both (**1**) and (**2**) are useful precursors to other organopalladium species by ligand exchange reactions.

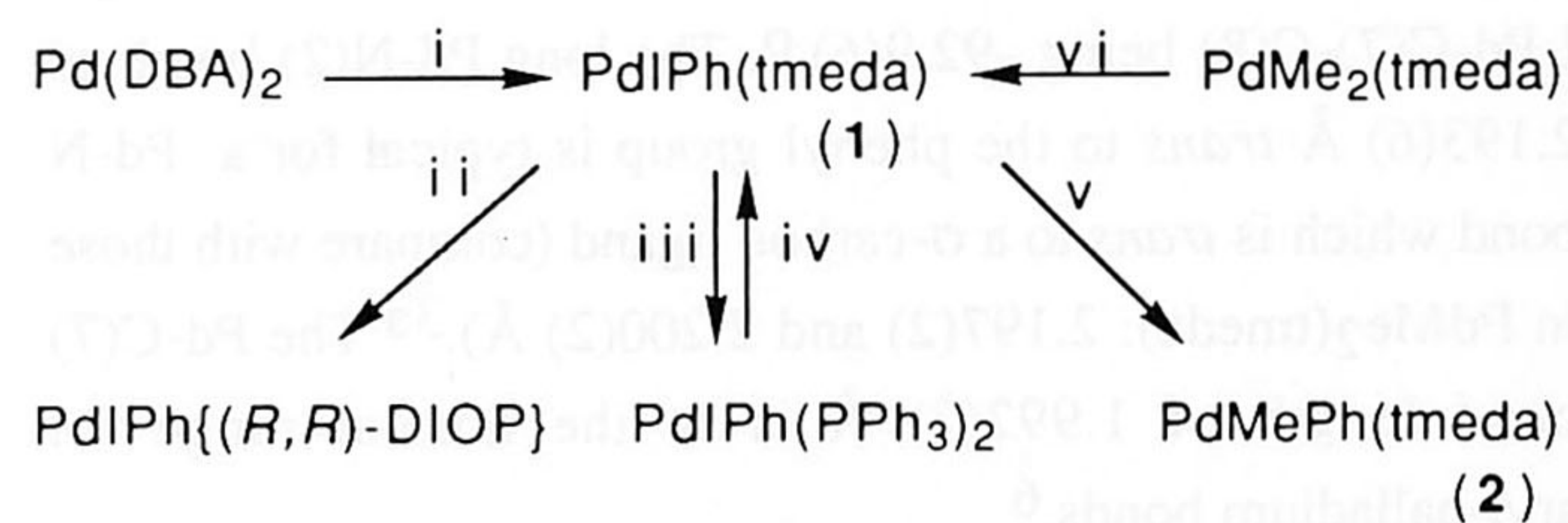
The use of simple amine ligands in organopalladium chemistry has been very limited, probably because palladium has often been regarded as a soft metal centre which requires soft ligands, like phosphines, for the stabilization of its organometallic complexes. However, PdMe₂(2,2'-bipyridine) has been known¹ since 1960 and more recently, stable organopalladium complexes with tertiary diamine ligands were prepared. Specific examples are Pd(CH₂)₄(tmeda)² and PdMe₂(tmeda)³ {tmeda = Me₂N(CH₂)₂NMe₂} in both of which the tmeda ligand is easily exchanged by 2,2'-bipyridine and mono- and diphosphines.

We now report an easy high-yield synthesis of PdIPh(tmeda) (**1**) and the mixed diorganopalladium compound PdMePh(tmeda) (**2**). These new aryl diamine palladium complexes are stable at 25 °C and can serve as convenient synthetic precursors for corresponding phosphine complexes. These properties make (**1**) and (**2**) very interesting complexes for current mechanistic studies on reductive elimination processes from palladium.

The complex PdIPh(tmeda) (**1**) is prepared in one step by the oxidative addition of iodobenzene to Pd(DBA)₂ {DBA = dibenzylideneacetone} in the presence of a slight excess of tmeda in tetrahydrofuran (THF) at + 40 °C (Scheme; route i).

The yellow-orange reaction mixture was filtered and the filtrate evaporated *in vacuo*. The residue was washed with diethyl ether (to remove DBA) leaving yellow-brown crystalline PdIPh(tmeda) (**1**)⁴ (75 %) which appeared indefinitely stable in air at room temperature.

The ¹H NMR spectrum of (**1**) shows only two singlets of the two NMe₂ groups. We believe that this is due to dynamic ring puckering, as observed earlier in PdMe₂(tmeda).^{3c} The two CH₂ groups appear as a complex AA'BB' pattern and the phenyl resonances as three well-separated multiplets.



Scheme. Reagents: i, tmeda, PhI, Et₂O, 75 %; ii, (R,R)-DIOP, THF, 75 %; iii, 2 PPh₃, THF, 90 %; iv, S₈, tmeda, THF, 75 %; v, MeLi, 0 °C, Et₂O, 85 %; vi, PhI, THF, 48 hr, 0-7 %.

Because of the unexpected stability of (**1**) and its unique feature of Pd-C(aryl) and Pd-N bonds in a non-cyclometallated arylpalladium complex containing a tertiary amine ligand we considered a molecular structure determination of this complex to be particularly worthwhile. Crystals of (**1**) suitable for an X-ray crystal structure analysis⁵ (see Figure) were obtained by recrystallization from hot benzene.

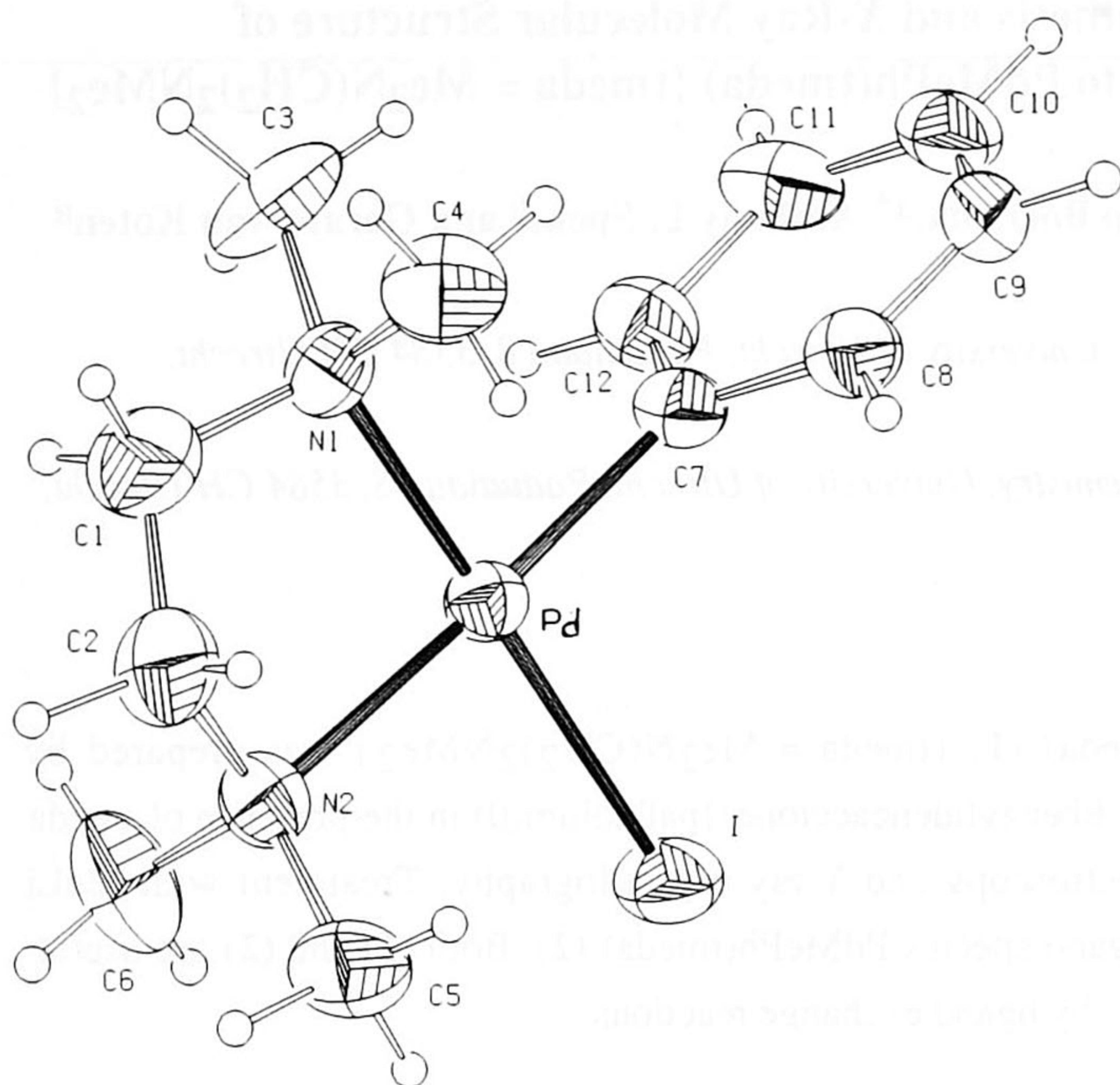


Figure. ORTEP drawing of a molecule of PdIPh(tmeda) (**1**) (30 % probability level). Selected bond lengths (Å), angles (°) and torsion angles (°): Pd-I 2.5703(8), Pd-N(1) 2.127(6), Pd-N(2) 2.193(6), Pd-C(7) 1.992(7), N(1)-Pd-N(2) 84.0(2), C(7)-Pd-I 87.4(2), C(7)-Pd-N(1) 92.8(3), I-Pd-N(2) 95.8(2), I-Pd-C(7)-C(8) -92.9(6), N(1)-C(1)-C(2)-N(2) -54(1).

The molecular geometry of (**1**) comprises a square-planar coordinated palladium atom with a bidentate tmeda ligand (\angle N-Pd-N 84.0(2) °) and mutually *cis*-positioned phenyl and iodide ligands. The phenyl group is orientated almost perpendicular to the coordination plane, the torsion angle I-Pd-C(7)-C(8) being -92.9(6) °. The long Pd-N(2) bond of 2.193(6) Å *trans* to the phenyl group is typical for a Pd-N bond which is *trans* to a σ -carbon ligand (compare with those in PdMe₂(tmeda): 2.197(2) and 2.200(2) Å).^{3a} The Pd-C(7) bond length of 1.992(7) Å is in the normal range for aryl-palladium bonds.⁶

Ligand exchange reactions using PdIPh(tmeda) (**1**) show it to be an excellent starting material for the synthesis of other iodo(phenyl)palladium complexes (Scheme; route ii and iii). For example, the reaction of (**1**) with one equivalent of (*R,R*)-4,5-*bis*-(diphenylphosphinomethyl)-2,2-dimethyl-1,3-

dioxolane {(*R,R*)-DIOP} affords PdIPh{(*R,R*)-DIOP} in 75 % yield,⁷ and the reaction with two equivalents of triphenylphosphine affords *trans*-PdIPh(PPh₃)₂ in 90 % yield. Interestingly, the latter compound, which is also available from the oxidative addition reaction of iodobenzene to Pd(PPh₃)₄,⁸ can be reconverted to PdIPh(tmeda) in 75 % yield by treatment of its THF solution with excess elemental sulfur and a slight excess of tmeda. Reactions ii and iii bear a close relationship to the ligand exchange reactions realised for Pd(CH₂)₄(tmeda)² and PdMe₂(tmeda).³

Another very interesting aspect of the chemistry of PdIPh(tmeda) is that with methyllithium in diethyl ether it is readily converted to the mixed diorgano complex PdMePh(tmeda) (**2**)⁹ which can be isolated as a pale grey solid in 85 % yield (scheme; route v). Complex (**2**) is, surprisingly, thermally more stable than the analogous *cis*-(methyl)(phenyl)*bis*-(phosphine)palladium complexes;¹⁰ the latter generally decompose rapidly in solution at temperatures above +20 °C. In fact solutions of (**2**) in acetone are sufficiently stable to obtain ¹H and ¹³C NMR spectra at room temperature and show no significant decomposition upon standing for hours, though these solutions do slowly turn darker.

This present new method for the formation of organopalladium amine complexes, i.e. oxidative addition of PhI to Pd(DBA)₂ and tmeda is complementary to other available methods. We reported earlier that compounds of the type PdXR(tmeda) can be prepared by the ready reaction of sp³-hybridized carbon halides (RX = methyl iodide and methyl, allyl and benzyl bromide) to PdMe₂(tmeda); this procedure involves formation of an intermediate palladium(IV) oxidative addition compound which then eliminates ethane exclusively.^{3c} However, this procedure with sp²-hybridized carbon halides, e.g. PhI and CH₂=CHBr, results in the slow formation of mainly PdXMe(tmeda) and in the case of PhI only a small amount (0-7 %) of the desired complex PdIPh(tmeda) (**1**) is obtained (scheme; route vi).

The utility of amine complexes like (**1**) and (**2**) has a wide scope. For example, the intermediates that have been proposed by Yamamoto *et al.*¹⁰ in reductive elimination processes in palladium catalysed C-C coupling reactions should be readily accessible as pure compounds by ligand exchange reactions with (**2**) (*viz* scheme; reactions ii and iii). Studies in this and related areas are in progress.

Acknowledgement

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- 4 M.p.: 170-171 °C (dec). C₁₂H₂₁IN₂Pd(426.63): calcd. C, 33.78; H, 4.96; N, 6.57; found C, 34.20; H, 4.82; N, 6.14. ¹H NMR (200 MHz, CDCl₃): δ 2.29 (6H, s, NMe₂), 2.67 (6H, s, NMe₂), 2.60 (4H, AA'BB', -CH₂-), 6.78 (1H, t, *p*-Ph), 6.90 (t, 2H, *m*-Ph), and 7.23 (d, 2H, *o*-Ph); ¹³C NMR (50 MHz, CDCl₃) δ 49.62, 49.80 (NMe₂); 58.13, 62.03 (-CH₂-); 122.54, 126.42, 136.35, 144.68 (Ph).
- 5 Crystal data for C₁₂H₂₁IN₂Pd, M = 426.6, tetragonal, space group P4₂/n, *a* = *b* = 19.082(1), *c* = 8.5367(5) Å, *U* = 3108.4(3) Å³, *Z* = 8, *D_c* = 1.823 g.cm⁻³, *F*(000) = 1648, *T* = 295 K, λ = 0.71073 Å, μ(Mo-Kα) = 31.3 cm⁻¹. Data (7561 reflections, θ_{max} = 27.5 °) were collected with an Enraf-Nonius CAD-4 diffractometer and corrected for absorption (DIFABS). The structure was solved with standard Patterson and Fourier methods (SHELXS) and refined by full-matrix least-squares (SHELX 76) to R = 0.050 (wR = 0.042) for 2315 reflections with *I* > 2.5 σ(*I*). Atomic coordinates, thermal parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.
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- 7 (a) M. Hodgson, D. Parker, R. J. Tayler and G. Ferguson, *J. Chem. Soc., Chem. Commun.* 1309 (1987). (b) W. de Graaf, J. Boersma, C. J. Elsevier and G. van Koten, submitted to *J. Organomet. Chem.*
- 8 P. Fitton, M. P. Johnson and J. E. Mc Keon, *J. Chem. Soc., Chem. Commun.* 6 (1968).
- 9 PdMePh(tmeda): M.p.: 113 °C (dec). ¹H NMR (200 MHz, CD₃COCD₃) δ -0.22 (3H, s, PdMe); 2.26 (6H, s, NMe₂); 2.47 (6H, s, N'Me₂); 2.7 (4H, br. d, -CH₂-); 6.70 (1H, t, *p*-H, Ph); 6.80 (2H, t, *m*-H, Ph); 7.36 (2H, d, Ph). ¹³C NMR (50 MHz, CD₃COCD₃) δ -7.8 (PdMe); 48.5 (NMe₂, N'Me₂); 59.9, 60.5 (-CH₂-); 121.2, 136.3, 138.6 (Ph).
- 10 F. Ozawa, K. Kurihara, M. Fujimori, T. Hidaka, T. Toyoshima and A. Yamamoto, *Organometallics* **8**, 180 (1989).