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Synthetic and computational studies of the palladium(IV) system Pd(alkyl)-(aryl)(alkynyl)(bidentate)(triflate) exhibiting selectivity in C–C reductive elimination[†]

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Synthetic routes to methyl(aryl)alkynylpalladium(IV) motifs are presented, together with studies of selectivity in carbon-carbon coupling by reductive elimination from Pd^{IV} centres. The iodonium reagents $IPh(C \equiv CR)(OTf)$ (R = SiMe₃, Bu^t, OTf = O₃SCF₃) oxidise Pd^{II}Me(p-Tol)(L₂) (1-3) [L₂ = 1,2-bis-(dimethylphosphino)ethane (dmpe) (1), 2,2'-bipyridine (bpy) (2), 1,10-phenanthroline (phen) (3)] in acetone-d₆ or toluene-d₉ at -80 °C to form complexes Pd^{IV}(OTf)Me(*p*-Tol)(C \equiv CR)(L₂) [R = SiMe₃, $L_2 = dmpe (4), bpy (5), phen (6); R = Bu', L_2 = dmpe (7), bpy (8), phen (9)] which reductively eliminate$ predominantly (>90%) p-Tol-C \equiv CR above ~-50 °C. NMR spectra show that isomeric mixtures are present for the Pd^{IV} complexes: three for dmpe complexes (4, 7), and two for bpy and phen complexes (5, 6, 8, 9), with reversible reduction in the number of isomers to two occurring between -80 °C and -60 °C observed for the dmpe complex 4 in toluene-d₈. Kinetic data for reductive elimination from $Pd^{IV}(OTf)Me_{(p-Tol)}(C \equiv CSiMe_3)(dmpe)$ (4) yield similar activation parameters in acetone-d₆ $(66 \pm 2 \text{ kJ mol}^{-1}, \Delta H^{\ddagger} 64 \pm 2 \text{ kJ mol}^{-1}, \Delta S^{\ddagger} -67 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1})$ and toluene-d₈ ($E_a 68 \pm 3 \text{ kJ mol}^{-1}$, ΔH^{\ddagger} 66 ± 3 kJ mol⁻¹, ΔS^{\ddagger} -74 ± 3 J K⁻¹ mol⁻¹). The reaction rate in acetone-d₆ is unaffected by addition of sodium triflate, indicative of reductive elimination without prior dissociation of triflate. DFT computational studies at the B97-D level show that the energy difference between the three isomers of 4 is small (12.6 kJ mol⁻¹), and is similar to the energy difference encompassing the six potential transition state structures from these isomers leading to three feasible C-C coupling products (13.0 kJ mol⁻¹). The calculations are supportive of reductive elimination occurring directly from two of the three NMR observed isomers of 4, involving lower activation energies to form p-ToIC=CSiMe₃ and earlier transition states than for other products, and involving coupling of carbon atoms with higher s character of σ -bonds $(sp^2 \text{ for } p\text{-Tol}, sp \text{ for } C \equiv C - SiMe_3)$ to form the product with the strongest C-C bond energy of the potential coupling products. Reductive elimination occurs predominantly from the isomer with $Me_3SiC \equiv C \text{ trans to OTf. Crystal structure analyses are presented for Pd^{II}Me(p-Tol)(dmpe) (1),$ $Pd^{II}Me(p-Tol)(bpy)$ (2), and the acetonyl complex $Pd^{II}Me(CH_2COMe)(bpy)$ (11).

Introduction

Early compelling evidence for the existence of bis(phosphine)triorganopalladium(IV) complexes of configuration 'PdXC₃P₂', but lacking spectroscopic evidence,¹ has been followed by electrochemical studies² indicating irreversible oxidation (Pd^{II}/Pd^{III}) for *trans*- $[Pd^{II}(C \equiv CR)_2(PBu_3)_2]^2$ and trans-[Pd^{II}Cl(C=CR)-(PPh₃)₂] species,^{2b} isolation of binuclear Pd^{III} complexes,³ and characterisation of several mono(phosphine)palladium(IV) species '[PdC₃N₂P]^{+,4} exemplified by the X-ray structural analysis for [Pd^{IV}Me₃(phen)(PMe₂Ph)](OTf) (phen = 1,10-phenanthroline, OTf = triflate),^{4a} and isolation of a $(PdC_2N_3P)^{2+}$ complex $[Pd^{IV}(CH_2CMe_2-o-C_6H_4-C,C')(Tp-N,N',N'')(PMe_3)]$ - $(NO_3)_2$ [Tp = tris(pyrazol-1-yl)borate].⁵ The complex *trans*-[Pd- $(C \equiv C-o-Tol)_2(PMe_2Ph)_2]^6$ reacts with the iodonium reagent IPh₂(OTf) to form (o-TolC=C)₂ and o-TolC=CPh), with IPh- $(C \equiv CR)(OTf)$ (R = Bu^t, SiMe₃) to form (*o*-TolC \equiv C)₂ and o-TolC \equiv C–C \equiv CR), and with IPhCl₂ to form o-TolC \equiv CCl; for these reactions spectroscopic evidence for intermediates is

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present but is considered insufficient to definitively characterize possible higher oxidation state intermediates.

We have recently reported that ¹H NMR studies in acetone-d₆ of the reaction of $Pd^{II}Me_2(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane] with the iodine(III) oxidant IPh(C=CSiMe₃)(OTf) at -50 °C, followed by addition of sodium iodide at -50 °C, indicate the formation of unstable Pd^{IV}IMe₂(C=CSiMe₃)(dmpe) containing the 'fac-[PdIC₃P₂]' configuration^{7a} related to the early reports by Stille and coworkers where spectroscopic evidence was not accessible.¹ The platinum(IV) analogue was isolated and, following subsequent studies of the detection of Pt^{IV}(OTf)Me(*p*-Tol)(C=CSiMe₃)(dmpe) in solution and X-ray structural characterisation of fac-[Pt^{IV}IMe(p-Tol)(C=CSiMe₃)-(dmpe)],^{7b} in this report we have explored the reactivity of $Pd^{II}Me(p-Tol)(L_2)$ (L₂ = dmpe, bpy, phen) (bpy = 2,2'-bipyridine) toward IPh(C=CR)(OTf) (R = Bu^t, SiMe₃) at -80 °C. Unstable Pd^{IV} complexes are detected by ¹H and ³¹P NMR, and the selectivity in reductive elimination at -60 °C examined from the d₆ 'PdOC₃L₂' centres containing three different organyl groups (sp^3, sp^2, sp) that are unrestrained by, for example, being part of chelating groups. This situation represents, apparently, a unique opportunity to examine reductive elimination selectivity under very mild and unrestrained conditions, and we have complemented the NMR studies with DFT calculations to further probe the selectivity in reductive elimination and the nature of transition states.

Experimental

Air-sensitive materials were handled under an argon atmosphere using standard Schlenk techniques, and all solvents were dried and distilled by conventional methods prior to use. The complexes $Pd^{II}Me(p-Tol)(L_2)$ ($L_2 = dmpe(1)$, ^{8a} bpy (2), phen (3)^{8b}) and $IPh(C \equiv CR)(OTf)$ (R = SiMe₃, Bu^t)⁹ were prepared as previously reported. NMR spectra were recorded on a Varian Unity Inova 400 WB spectrometer. ¹H NMR spectra were secondary-referenced to residual solvent signals; assignments of all resonances were supported by two-dimensional NMR spectroscopy (COSY, HMBC). ³¹P NMR spectra were externally referenced to 85% H₃PO₄.

GCMS analyses were carried out on a Varian 3800 GC coupled to a Varian 1200 triple quadrupole mass spectrometer in single quadrupole mode. A Varian 'Factor Four' VF-5 ms (30 m \times 0.25 mm internal diameter and 0.25 um film) column was used. Injections of 1 µL were made using a Varian CP-8400 autosampler and a Varian 1177 split/splitless injector at 220 °C with a split ratio of 30:1. The ion source was at 220 °C, and the transfer line at 290 °C. The carrier gas was helium at 1.2 mL min⁻¹ using constant flow mode. The column oven was held at 50 °C for 2 min then ramped to 290 °C at 8° min⁻¹. The range from m/z 35 to 550 was scanned 3 times per second. GC-FID was carried out on a Varian 450-GC with 1177 split/splitless injector using similar conditions to the above, except that the carrier gas was nitrogen. The FID response factors for trimethylsilvlacetylene, and *n*-heptadecane were determined from a solution of known concentration, employing where necessary the 'effective carbon number' concept of known negative effects on FID response.10,11

Oxidation studies

A solution of IPh(C=CR)(OTf) $(4.17 \times 10^{-2} \text{ mmol})$ in acetoned₆ or toluene-d₈ (0.5 mL) at -80 °C was added to a solution of PdMe(*p*-Tol)(L₂) (L₂ = dmpe, bpy, phen) $(4.17 \times 10^{-2} \text{ mmol})$ in acetone-d₆ or toluene-d₈ (1.0 mL) in a round-bottomed flask at -80 °C in an acetone slush bath, and an aliquot immediately transferred to a pre-cooled NMR tube and quickly inserted into the NMR probe equilibrated at -80 °C. As all spectra were obtained at -80 °C some resonances are broad and not well resolved, in particular for ³¹P spectra.

Pd(OTf)Me(*p*-Tol)(C=CSiMe₃)(dmpe) (4). ¹H NMR (400 MHz, acetone-d₆): δ 8.51 (d, 2H, H(2,6)_{Tol}), 8.44 (d, 2H, H (2,6)_{Tol}), 8.34 (d, 2H, H(2,6)_{Tol}), 7.81 (t, 2H, H(3,5)_{Tol}), 7.78 $(m, 2H, H(3,5)_{Tol}), 7.63$ $(m, 2H, H(3,5)_{Tol}), 2.37$ (s, 3H, 3H)(CH₃)_{Tol}, 2.21 (s, 3H, (CH₃)_{Tol}, 2.17 (s, 3H, (CH₃)_{Tol}, 1.82–1.46 (m, overlapping for PCH₂, PCH₃), 0.40 (bs, 3H, PdCH₃), 0.35 (bs, 3H, PdCH₃), 0.32 (bs, 3H, PdCH₃), 0.16 (s, 9H, Si(CH₃)₃) 0.12 (bs, 18H, Si(CH₃)₃). ³¹P NMR (162 MHz, acetone-d₆): δ 41.25, 34.78 (d, $J_{PP} = 27$), 30.70 (d, $J_{PP} = 21$ Hz), 26.15 (d, J_{PP} = 21 Hz), 23.61 (d, J_{PP} = 21 Hz), 23.22 (d, J_{PP} = 26 Hz). ¹H NMR (400 MHz, toluene-d₈): δ): δ 7.97 (m, 2H, H(2,6)_{Tol}), 9.81 (m, 2H, H(2,6)_{Tol}), 7.31(d, 2H, H(3,5)_{Tol}), 7.18 (d, 2H, H $(3,5)_{Tol}$, 2.40 (s, 3H, $(CH_3)_{Tol}$), 2.32 (s, 3H, $(CH_3)_{Tol}$), 0.84-0.68 (m, overlapping for PCH₂, PCH₃, PdCH₃), 0.64 (bs, 18H, Si(CH₃)₃). ³¹P NMR (162 MHz, toluene) δ 23.40 (d, J_{PP} = 10 Hz) 20.83 (bs), 20.16 (d, $J_{PP} = 10$ Hz).

Pd(OTf)Me(*p***-Tol)(C≡CSiMe₃)(bpy) (5).** ¹H NMR (400 MHz, acetone-d₆): δ 9.19 (d, 2H, bpy), 8.97 (d, 2H, bpy), 8.96–8.91 (m, 8H, overlapping bpy and tolyl), 8.44–8.36 (m, 8H, overlapping bpy and tolyl), 8.00–7.90 (m, 4H, bpy), 2.31 (s, 3H, (CH₃)_{Tol}, 2.24 (s, 3H, (CH₃)_{Tol}), 1.87 and 1.65 (bs, 6H, PdCH₃), 0.10 and 0.07 (s, 18H, Si(CH₃)₃).

Pd(OTf)Me(*p***-Tol)(C≡CSiMe₃)(phen)** (6). ¹H NMR (400 MHz, acetone-d₆): 9.71 (d, 2H, phen), 9.46 (d, 2H, phen), 9.15 (d, 2H, phen), 9.01–8.94 (m, 8H, phen and tolyl), 8.86 (d, 2H, phen), 8.31–8.25 (m, 6H, phen and tolyl), 8.21 (d, 2H, tolyl), 2.30 and 2.10 (s, 3H, $(CH_3)_{Tol}$), 1.80 (s, 3H, PdCH₃), 1.66 (s, 3H, PdCH₃), 0.08 and 0.03 (bs, 18H, Si(CH₃)₃).

Pd(OTf)Me(*p***-Tol)(C≡CBu')(dmpe)** (7). ¹H NMR (400 MHz, acetone-d₆): 8.48–8.44 (dd, 4H, tolyl), 8.36 (d, J = 8Hz, 2H, tolyl), 7.65–7.61 (m, 4H,), 7.46–7.40 (m, 2H), 2.19, 2.15, 2.13 (s, 9H, (CH₃)_{Tol}), 1.80–1.55 (m, 48H, PCH₂, PCH₃), 1.47–1.40 and 1.34–1.30 (m, 27H, C(CH₃)₃, 1.07, 1.03, 1.01 (s, 9H, PdCH₃); ³¹P NMR (162 MHz, acetone-d₆) δ; 32.46 (d, J_{PP} = 26), 29.36 (d, $J_{PP} = 26$ Hz), 26.61 (d, $J_{PP} = 26$ Hz), 23.42 (d, $J_{PP} = 21$ Hz), 21.05 (d, $J_{PP} = 19$ Hz), 19.85 (d, $J_{PP} = 21$ Hz).

Pd(OTf)Me(*p***-Tol)(C≡CBu')(bpy) (8).** ¹H NMR (400 MHz, acetone-d₆): 9.37 (d, 2H, bpy), 9.04 (d, 2H, bpy), 8.88 (t, 4H, bpy), 8.75–8.68 (m, 4H, bpy) 8.48–8.39 (m, 4H, bpy and tolyl), 8.04–7.99 (m, 4H, bpy and tolyl), 7.90–7.86 (m, 4H, bpy and tolyl), 2.30 (s, 3H, $(CH_3)_{Tol}$), 2.01 (s, 3H, $(CH_3)_{Tol}$)), 1.83 and 1.62 (bs, 6H, PdCH₃) 1.14 (bs, 18H, $C(CH_3)_3$).

Pd(OTf)Me(*p***-Tol)(C≡CBu**^{*t*})(**phen) (9).** ¹H NMR (400 MHz, acetone-d₆): 9.75 (d, 2H, phen), 9.45 (d, 2H, phen), 9.08–8.97

(m, 8H, phen and tolyl), 8.84 (bd, 4H, tolyl), 8.41 (bs, 2H, phen), 8.31 (bs, 2H, phen), 8.19 (d, 2H, tolyl), 7.87 (d, 2H, tolyl), 2.30 (s, 3H, $(CH_3)_{Tol}$), 1.90 (s, 3H, $(CH_3)_{Tol}$), 1.68, 1.46 (bs, 6H, PdC H_3), 1.11 (bs, 18H, C(CH_3)₃).

Decomposition studies

The reaction mixtures (2.48 M) in acetone-d₆ or toluene-d₈, obtained as above, were transferred to an NMR tube and immediately inserted into the NMR probe which was maintained at -80 °C. The decomposition of Pd^{IV} complexes was monitored by the disappearance of the H_{ortho} resonances of the tolyl group which were better resolved from other resonances, and the rate of decomposition was calculated from the combined integration of these resonances. First order rate constants k_{obs} (sec⁻¹) were obtained from plots of $\ln(A_o/A_1)$ versus time at specific temperatures. The overall reaction order was determined using different concentrations of the complex (3.71 × 10⁻² M, 2.48 × 10⁻² M, 1.65 × 10⁻² M and 1.35×10^{-2} M); plots of k_{obs} against concentration of the complexes gave a straight line through the origin indicating first order behaviour.

The influence of temperature on the rate of decomposition was investigated by monitoring the reaction at different temperature $(-40^{\circ}, -35^{\circ}, -30^{\circ}, -25^{\circ}, -20^{\circ} \text{ in acetone-d}_6 \text{ and } -35^{\circ}, -25^{\circ}, -20^{\circ}, -15^{\circ} \text{ in toluene-d}_8)$ with a constant concentration of the complex $(2.48 \times 10^{-2} \text{ M})$. Energies of activation were calculated from Arrhenius plots (ln $k_{obs} = \ln A_o - E_a/RT, R = 8.314 \text{ J mol}^{-1}$ K); and enthalpies and entropies of activation were obtained from Eyring plots (ln $(k_{obs}/T) = \ln(\kappa/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$ ($\kappa = 1.38 \times 10^{-23} \text{ J K}^{-1}, h = 6.626 \times 10^{-34} \text{ J s}$).

Structural determinations

Crystals of **1** and **2** were obtained directly from the preparations, and complex **11** was obtained as a component of decomposition of **5** after an acetone-d₆ solution was left for several days at -40 °C. Data for **1**, **2** and **11** were collected at -173 °C for crystals mounted on a Hampton Scientific cryoloop at the MX1 beamline of the Australian Synchrotron.¹² The structures were solved by direct methods with SHELXS-97,¹³ and visualized using X-SEED.¹⁴ All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C–H distances of 0.95 (sp²C–H), 0.99 (CH₂), 0.98 Å (CH₃). The thermal parameters of all hydrogen atoms were estimated as $U_{iso}(H) = 1.2U_{eq}(C)$ except for CH₃ where $U_{iso}(H) = 1.5U_{eq}(C)$. A summary of crystallographic data given below.

Crystal data for 1: $C_{14}H_{26}P_2Pd$, M = 362.69, monoclinic, a = 8.782(2), b = 18.624(3), c = 10.664(2) Å, $\beta = 107.991(16)^{\circ}$, V = 1658.9(6) Å³, T = 100 K, space group $P2_1/n$ (no. 14), Z = 4, 17 001 reflections measured, 2520 unique ($R_{int} = 0.0926$), 2152 > $4\sigma(F)$, R = 0.0449 (observed), $R_w = 0.1131$ (all data). Crystal data for 2: $C_{18}H_{18}N_2Pd$, M = 368.74, monoclinic, a = 47.366(2), b = 8.4950(9), c = 25.0650(15) Å, $\beta = 115.3600(10)^{\circ}$, V = 9113.6(12) Å³, T = 100 K, space group C2/c (no. 2), Z = 24, 46 306 reflections measured, 6953 unique ($R_{int} = 0.0324$), 6758 > $4\sigma(F)$, R = 0.0458 (observed), $R_w = 0.1075$ (all data). Crystal data for 11: $C_{14}H_{16}N_2OPd$, M = 334.69, triclinic, a = 7.6740(7),

b = 9.1480(7), c = 9.4860(6) Å, α = 84.0070(10), β = 80.678(5), $γ = 79.390(4)^\circ, V = 643.99(9)$ Å³, T = 100 K, space group $P\bar{1}$ (no. 2), Z = 2, 6554 reflections measured, 1750 unique ($R_{int} = 0.0786$), 1694 > 4σ(F), R = 0.0385 (observed), $R_w = 0.0978$ (all data).

Computational details

The equilibrium molecular structures as well as transition state geometries were optimized using the hybrid density functional B97-D which includes dispersion energy corrections.¹⁵ For the geometry optimisations, the effective core potentials of Hay and Wadt with double- ζ valence basis sets (LANL2DZ)¹⁶ were chosen to describe Pd, and the 6-31G(d) basis set was used for other atoms.¹⁷ Frequency calculations were performed to confirm that optimized structures were minima or saddle points. All transition structures contained exactly one imaginary frequency and were linked to reactants, products, or intermediates using the intrinsic reaction coordinate (IRC) algorithm.¹⁸ To test the effect of polarization and diffusion functions, single point energy calculations were carried out for all structures with a larger basis set, LANL2TZ+(3f) basis set on Pd (including diffuse functions and polarisation functions¹⁶ (see ESI[†]), and the 6-311+G(2d,p) basis set on other atoms. All thermodynamic data were calculated at the standard state (298.15 K and 1 atm). Nonexplicit solvent effects were also tested with the IEFPCM (SCRF) model¹⁹ using acetone and toluene as solvents. All final energies reported in this manuscript are with the larger basis set and include acetone solvent corrections. All calculations were carried out with the Gaussian09 suite of codes.²⁰ All Mulliken, NBO electron densities and bonding analyses were analysed using the natural bond order (NBO) technique.²¹ The NBO analysis describes donor-acceptor interactions according to a second-order perturbation theory.

Boltzmann population distributions, at -80, -35, and 25.15 °C, were obtained by normalizing the individual population distribution calculated by using the equation $N_i = \exp(-\Delta G/RT)$; where ΔG is the relative free energy difference from the most stable isomer. Individual rate constants were calculated by using the $k(T) = (k_{\rm B}T/hc^{\rm o}) \exp(-\Delta G/RT)$ from transition state theory.

Results

Synthesis and characterisation of Pd^{IV} complexes

¹H NMR studies at -80 °C indicated that complexes are formed according to Scheme 1, where Pd^{IV} complexes are present as a mixture of isomers, and, for the dmpe complex 4 in toluene-d₈,



Scheme 1

the ratio of isomers is altered reversibly between -80 and 60 °C (see below).

¹H and ³¹P{¹H} NMR spectra at -80 °C in acetone-d₆ indicate the presence of three isomers for the dmpe complexes and two isomers for bpy and phen complexes, in approximately equal ratio based upon ¹H NMR assignments for all PdMe, *p*-Tol, SiMe₃, and some bpy and phen resonances, *e.g.* Fig. 2 illustrates the presence of three isomers for 4 (three H_{ortho} and H_{meta} environments for the *p*-Tol group (confirmed by COSY spectra)) and 7 (six phosphorus environments). There is a general feature of downfield shifts for ¹H NMR resonances of bpy (~0.5–1 ppm), phen (~0.5 ppm), H_{ortho,meta} of *p*-Tol (~0.6–1.5 ppm), PMe (0.2–0.8 ppm), and PdMe (~0.3–1.5 ppm), similar to those reported on oxidative addition of benzyl bromide to PdMePh(bpy)²² and PdMe(*p*-Tol)(phen).^{8b}

Complex 4 was found to exhibit ¹H NMR spectra that are more easily interpreted and monitored during reactions, in particular the upfield trimethylsilyl resonance, well resolved $H_{ortho,meta}$ resonances (Fig. 2(a)), and the availability of ³¹P NMR resonances, and thus this complex was selected for further decomposition studies. In acetone-d₆ and toluene-d₈, the initial ratio of isomers at -80 °C is $\sim 1:1:1$, but the isomer with the most downfield H_{ortho} diminished to give two isomers in ~1:1 ratio. In toluene-d₈, at -80 °C the process is very slow, and only proceeds rapidly almost to completion at -60 °C. This process is reversible in toluene-d₈ indicating facile conversion of one isomer to (i) both of the other isomers, or (ii) one of the other isomers and interconversion between these, or (iii) occurrence of both (i) and (ii). The H_{meta} resonances of the isomers of 4 in toluene-d₈ are coincident with the solvent resonances, unlike the well resolved spectrum in acetone-d₆ (Fig. 2a). The *t*-butylethynyl analogue (7) lacks sufficient resolution of Hortho and Hmeta resonances to study the assumed occurrence of equilibria.

Decomposition of Pd^{IV} complexes

Reductive elimination above ~ -50 °C was examined by ¹H NMR spectroscopy and GC-MS. The complexes as pale yellow

solutions in acetone-d₆ or toluene-d₈ decomposed above \sim -50 °C to form light brown solutions containing *p*-Tol-C=CSiMe₃ as the dominant organic product (>90%) and minor quantities of *p*-Tol-Me and Me-C=CSiMe₃ (Scheme 1). Complex ¹H NMR spectra have not permitted characterisation of the initial palladium containing products of reductive elimination, apparently owing to subsequent decomposition of the assumed products 'PdR(L₂)(OTf)'. Partial decomposition to Pd⁰ species is anticipated to lead to oxidative addition reactions with iodobenzene (byproduct of reaction of IPh(C=CR)(OTf) with 1–3) and transfer of organyl groups between Pd^{II} species to generate several palladium containing products. This process would also account for the observed presence of minor organic products (Ph–Ph, *p*-Tol-Ph). Supportive of this interpretation, the amount of these organic products increases overnight.

An acetonylpalladium(II) complex, PdMe(CH₂COMe)(bpy) (11) was detected amongst other products by X-ray crystallographic analysis from the decomposition of **4** in acetone-d₆ (Fig. 1(c)). Acetonylpalladium(II) complexes are known to be readily formed on the reaction of chloropalladium(II) complexes with acetone in the presence of hydroxide²³ or on direct reaction of hydroxopalladium(II) complexes with acetone.²⁴ Platinum(II) complexes may be similarly formed,^{23,25} PtCl₂(NCMe)₂ reacts with bpy in acetone under reflux in air to form PtCl(CH₂COMe)-(bpy),²⁶ and the cyclohexyne complex Pt⁰(η^2 -C₆H₈)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) reacts with acetone/water to form the cyclohexenyl complex Pt^{II}(CH₂COMe)(η^1 -C₆H₉)-(dppe).²⁷

Kinetic studies of decomposition of Pd^{IV} complexes

To examine the mechanism of decomposition and the potential role of triflate dissociation from palladium($_{IV}$) complexes of the type formed here, kinetic studies of the decomposition of Pd(OTf)Me(*p*-Tol)(C=CSiMe₃)(dmpe) (4) at -25 °C were undertaken in the absence and presence of sodium triflate. Identical results were obtained on ¹H NMR monitoring the loss of combined H_{ortho,meta} resonances in the absence or presence of



Fig. 1 ORTEP representations of the structures of (a) PdMe(p-Tol)(dmpe) (1), PdMe(p-Tol)(bpy) (2) (one of three crystallographically independent molecules), and (c) $PdMe(CH_2COMe)(bpy)$ (11). Displacement ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for PdMe(p-Tol)(dmpe) (1): Pd(1)-C(1, 2) 2.093(6), 2.058(5); Pd(1)-P(1, 2) 2.3000(14), 2.903(14); C(1)-Pd(1)-C(2) 86.8(2), C(1)-Pd(1)-P(1, 2) 175.49(19), 92.64(16); C(2)-Pd(1)-P(1, 2) 94.41(14), 177.77(17); P(1)-Pd(1)P(2) 85.99(5). (b) PdMe(p-Tol)(bpy) (2): Pd(1n)-C(1n) 2.051(6), 2.044(6), 2.039(6); Pd(1n)-C(2n) 1.994(5), 2.010(5), 2.003(5); Pd(1n)-N(1n) 2.135(4), 2.139(5), 2.140(5); Pd(1n)-N(2n) 2.121(4), 2.138(5), 2.138(4); C(1n)-Pd(1n)-C(2n) 87.6(2), 87.7(2), 88.4(2); C(1n)-Pd(1n)-N(1n) 174.68(19), 172.8(2), 172.6(2); C(1n)-Pd(1n)-N(2n) 98.07(19), 95.7(2), 96.2(2); C(2n)-Pd(1n)-N(1n) 97.30(19), 99.4(2), 98.56(19); C(2n)-Pd(1n)-N(2n) 172.03(19), 173.66(19), 171.01(19); N(1n)-Pd(1n)-N(2n) 77.28(17), 77.32(17), 77.30(17). (c) $PdMe(CH_2COMe)(bpy)$ (11): Pd(1)-C(1, 2) 2.036(5), 2.082(5); Pd(1)-N(1, 2) 2.137(4), 2.111(4); C(1)-Pd(1)-C(2) 88.5(2), C(3)-C(2, 4) 1.462(7), 1.520(7); C(3)-O(1) 1.237(5), C(1)-Pd(1)-N(1, 2) 172.98(15), 95.63(18); C(2)-Pd(1)-N(1, 2) 98.24(17), 175.22(14); N(1)-Pd(1)-N(2) 77.77(14), Pd(1)-C(2)-C(3) 101.4(3), C(2)-C(3)-C(4) 118.5(4), C(2)-C(3)-O(1) 123.9(4), C(4)-C(3)-O(1) 117.6(4).





Fig. 2 (a) ¹H NMR showing H_{ortho} and H_{meta} resonances of the *p*-tolyl group for Pd(OTf)Me(*p*-Tol)(C=CSiMe₃)(dmpe) (4) in acetone-d₆ at -80 °C, and (b) ³¹P NMR spectra for Pd(OTf)Me(*p*-Tol)(C=CBu')-(dmpe) (7) in acetone-d₆ at -80 °C.

NaOTf (×3, ×5 excess) at -25 °C ($k_{obs} 2.5 \times 10^{-3} \text{ s}^{-1}$ at 2.48 × 10^{-2} M [Pd^{IV}]). If triflate dissociates prior to reductive elimination, reaction would be anticipated to be retarded by the presence of additional triflate. The concentration dependence of k_{obs} indicates first-order behavior, and Arrhenius and Eyring plots (ESI†) allowed determination of E_a , ΔH^{\ddagger} , and ΔS^{\ddagger} , based on dated collected at -40 to -15 °C for **4** in acetone-d₆ ($E_a 66 \pm 2 \text{ kJ mol}^{-1}$, $\Delta H^{\ddagger} 64 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger} -67 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$) and toluene-d₈ ($E_a 68 \pm 3 \text{ kJ mol}^{-1}$, $\Delta H^{\ddagger} 66 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger} -74 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$). Similar values for activation parameters in acetone-d₆ (and toluene-d₈ are supportive of a non-dissociative pathway. Under identical conditions of concentration (2.48 × 10^{-3} M) and temperature (-35 °C), reaction is ~7 times faster in acetone-d₆ than toluene-d₈, most likely attributable to formation of a polar transition state implied by negative values for ΔS^{\ddagger} .

Computational studies

The reductive elimination pathways were investigated with density functional theory (DFT). For this study we chose to use the B97-D functional because this includes the effects of dispersion energy and should give a more accurate picture of the energetics when steric repulsion is involved, such as in the systems studied here.²⁸ We have also compared the results obtained with a number of other density functionals and these comparisons (ESI[†]) emphasise the importance of including the effects of dispersion energy.

We considered various reductive elimination reactions starting from the three observed isomers of the Pd^{IV} reactant (Fig. 3). Reductive elimination of equatorial substituents *trans* to the bidentate phosphine donors is unlikely,²⁹ and calculations for elimination by this process indicated that these processes would be very slow, having a high activation energy (ESI⁺).



Fig. 3 Relative energy surfaces for B97-D concerted process.

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We have calculated three pairs of reductive elimination products, corresponding to the observed organic species and the assumed Pd^{II}(OTf)R(dmpe) products. There is some uncertainty in the structures of the Pd^{II} products since they could not be detected spectroscopically, and are potentially unstable with respect to decomposition. As the decomposition of 4 does not involve triflate dissociation, ΔE values are considered appropriate for estimation of relative energies of species.

The geometries of the six transition states shown in Fig. 3 are as expected, with the extra interest of an α -agostic Pd–H reaction as shown for 4c TS3. There are two transition structures leading to each pair of products: 4b TS1 and 4c TS1 lead to the formation of p-Tol-C=C-SiMe₃, 4a_TS2 and 4b_TS2 lead to Me-C=C-SiMe₃, and 4a TS3 and 4c TS3 lead to p-Tol-Me. We note that the lowest energy isomer of the Pd^{IV} precursor (4a) does not lead to the major product, and that the lowest energy transition structure (4b TS1) does not lead to the lowest energy pair of products [1,4-dimethylbenzene and Pd(OTf)-(C=CSiMe₃)(dmpe)]. However, this may be explained by interconversion between isomers as detected by NMR spectroscopy (see above) demonstrating that kinetic studies above -50 °C involve decomposition from one or two of the three isomers. In addition, the lowest activation barriers leading to products from **4b** and **4c** lead to the observed product (*p*-TolC=CSiMe₃), *via* transition states that have characteristics suggestive of 'early transition states'. As shown in ESI (Table S4[†]), the geometries of the TS1 structures show much less change compared to the reactants (smaller changes in bond lengths) than the TS2 and TS3 structures. In addition, NBO analyses indicate that the population of the $d_{x^2-y^2}$ orbital (corresponding to the reductive elimination process) increases by only 0.15 and 0.14 electrons for formation of 4b TS1 and 4c TS1, compared to increases of 0.21, 0.20, 0.28 and 0.23 electrons for 4a TS2, 4b TS2, 4a TS3 and 4b_TS3 (Table S5[†]). This supports the interpretation of the TS1

structures as corresponding to early transition states.³⁰ In turn, the early transition states correspond to the preferred reaction pathways. In a similar manner, examination of the HOMO's most directly related to formation of the new C–C bond, *e.g. via* **4b_TS1**, indicate that there is a net gain in the binding energy ($\Delta\Delta E = -0.079 \text{ eV}$) compared with other possibilities, *e.g.* $\Delta\Delta E = +0.382$ for **4b_TS2** for formation of Me-C=C-SiMe₃ (Fig. 4).

These observations also clearly demonstrate the role of s character and directionality^{30,31} of the component orbitals during transition state formation. Thus, the coupling of the sp² and sp carbons requires only a small amount of structural rearrangement to form a bonding interaction, whereas the coupling of the sp³ and sp or sp² and sp³ carbons requires a greater rearrangement in order to achieve a bonding overlap of molecular orbitals (ESI†). The amount of geometric deformation also corresponds with the strength of the C–C bond formed in the reductive elimination reaction, where a lesser deformation occurs for formation of the strongest C–C bond, 569.2 kJ mol⁻¹ for *p*-TolC≡C-SiMe₃ compared with 518.1 kJ mol⁻¹ for Me-C≡CSiMe₃ and 425.1 kJ mol⁻¹ for *p*-Tol-Me (Table S3†).

Although kinetic data indicate a pathway in which triflate dissociation does not occur, calculations for a dissociative pathway involving triflate dissociation were undertaken. These calculations show that the dissociative transition structures leading to the observed product are $32-50 \text{ kJ mol}^{-1}$ (ΔE^{\ddagger}) higher than for the non-dissociative pathway (Fig. 5, and ESI[†]).

We have also carried out a Boltzmann population analysis of isomers and effective rate constant for the various reductive elimination processes (Table 1). Irrespective of temperature, **4a** has the highest population, followed by **4b** and with a negligible amount of **4c**, which is consistent with observed two dominant pseudo-stable isomers. The observed $\sim 1 : 1$ ratio of two isomers is most likely due to a dynamic equilibrium between these isomers, as the process of interconversion of isomers was found



Fig. 4 HOMO's identified as significant in forming C–C bonds from 4a to give (a) *p*-Tol-C≡C-SiMe₃, and (b) Me-C≡C-SiMe₃.



Fig. 5 Relative energy surfaces (B97-D) for dissociative (and associative) pathways.

 Table 1
 Boltzmann population and rate constant analysis at various temperatures

Isomers	Temperature = $25.15 ^{\circ}C$		Temperature = -35.00 °C		Temperature = -80.00 °C	
	Normalized population	Effective rate constant (s^{-1})	Normalized population	Effective rate constant (s^{-1})	Normalized population	Effective rate constant (s ⁻¹)
4a 4a_TS1 4a_TS2 4a_TS3 4b 4b_TS1 4b_TS1 4b_TS2 4b_TS3 4c 4c_TS1 4c_TS1	9.36×10^{-1} 6.27×10^{-2} 9.5×10^{-4}	2.38 6.51×10^{1} 1.46×10^{2} 1.45×10^{3} 7.94×10^{1} 7.48×10^{-5} 5.30×10^{1} 5.03×10^{-7}	9.69×10^{-1} 3.11×10^{-2} 2.69×10^{-4}	$3.68 \times 10^{-3} 2.44 \times 10^{-1} 8.63 \times 10^{-1} 1.32 \times 10^{1} 3.93 2.15 \times 10^{-9} 3.21 9.64 \times 10^{-12} $	9.87×10^{-1} 1.34×10^{-2} 5.91×10^{-5}	$\begin{array}{c} 3.11 \times 10^{-6} \\ 6.22 \times 10^{-4} \\ 3.35 \times 10^{-3} \\ 8.55 \times 10^{-2} \\ 1.24 \times 10^{-2} \\ 9.91 \times 10^{-14} \\ 8.41 \times 10^{-7} \\ 3.36 \times 10^{-21} \end{array}$
4c_TS2 4c_TS3		5.03×10^{-7} 7.37		$\begin{array}{c} 9.64 \times 10^{-12} \\ 1.51 \times 10^{-2} \end{array}$		$\begin{array}{c} 3.36 \times 10^{-21} \\ 1.21 \times 10^{-9} \end{array}$

to be reversible (see above). Most interestingly, irrespective of temperature, the calculated effective rate for $4b_TS1$ (Table 1) is the highest, which is the transition structure leading to the formation of the observed major product. Again, the highest reaction rate is *via* $4b_TS1$, further supporting the interpretation of an early transition state for TS1. Thus, from the NMR study and theoretical investigation, it has become clear that there might be an equilibrium between isomers, and final reductive elimination predominantly takes place through one of the isomers. This situation can be represented by Scheme 2 showing the dominant pathway for product formation.



Scheme 2

Discussion

The synthetic results delineate a route to methyl(aryl)alkynylpalladium($_{IV}$) systems exhibiting the 'Pd^{IV}OC₃P₂' and 'Pd^{IV}OC₃N₂'

kernels, and examples of selectivity in reductive elimination from $d_6 MC_{sp^3}C_{sp^2}C_{sp}$ species where the organyl groups are not constrained, e.g. the sp^3 centre is a methyl group, the aryl group is unsubstituted at the ortho-positions, and palladacycles or palladocycles involving the organyl groups are not present. The observed decomposition pathway under mild conditions in solution for all of the complexes involves preferential formation of $C_{sp^2}-C_{sp}$ bonds, in this case *p*-Tol-C=CR (R = Bu^t, SiMe₃).

Reports to date of C-C reductive elimination at Pd^{IV} and related Pt^{IV} centres indicate either direct elimination from octahedral species or following dissociation of one donor to give a five-coordinate intermediate. Kinetic^{32a-c} and related studies^{32d,e} indicate dissociation of iodide from $Pd^{IV}IMe_3(L_2)$ (L₂ = bidentate nitrogen donor) in reductive elimination of ethane, 32a,d,e although this reaction proceeds without dissociation in the presence of high excess iodide concentration.^{32a} In the present system, where direct reaction from octahedral Pd^{IV}(OTf)Me-(p-Tol)(C=CR)(dmpe) is indicated, and has been examined at much lower temperature than other studies, the activation parameters are similar to those for ethane elimination from Pd^{IV}-IMe₃(bpy) when conducted at high iodide concentration in acetone-d₆, when reaction is non-dissociative (E_a 78 ± 11 kJ mol⁻¹, ΔS^{\ddagger} -53 \pm 25 J K⁻¹ mol⁻¹ in acetone), and are indicative of a polar transition state with six-coordinate metal centres.^{32a} Dissociation of PhSe⁻ is indicated for Pd^{IV}(SePh)₂Me₂(bpy)^{32c} and, for carboxylato- complexes $Pd^{IV}(O_2CR)_2(bzq-C_2N)_2$ (bzq = benzo[h]quinolinyl) dissociation of RCO₂⁻ occurs prior to C-O coupling but C-C coupling occurs directly from the octahedral species.^{32f} Computational studies are supportive of a five-coordinate intermediate $[Pd^{IV}I(C-C)(o-Tol)(PMe_3)]^+$ (C-C = phenylnorbornyl), in the reaction of o-TolI with $Pd(C-C)(PMe_3)_2$ to give an aryl-(o-Tol) coupled product C₇H₁₀C₆H₅-(o-Tol).³³ More extensive studies of C-C bond formation have been reported for platinum(IV), including experimental³⁴ and compustudies^{34k,35} tational supporting X^{-} dissociation for PtXMe₃(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane (X = $I_{,}^{34c,d}$ OAr, $O_2CR^{34e,g}$) and PtI₂(*p*-FC₆H₄)₂(dmpe);^{34k} pyridine dissociation from $[PtMe_3(dppe)(py)]^{+;34j}$ dissociation of one phosphine donor for PtXMe_3(dppe) (X = H, ^{34k,35d,e} Me^{34j,h,i,35d,e}); dissociation of one isonitrile for $PtMe_4(CNR)_2$ (R = Me, Xylyl);^{34b} and I⁻ loss slightly favoured for [PtI₄(CH=CIR)₂]^{2-,35b} and, for PtR_4L_2 (L = PMe₃, PH₃, PF₃, CO, NH₃), dissociation of L for R = Me,^{35*f*} and, for $R = CH=CH_2$, direct elimination when $L = PMe_3$ but both pathways competitive for other L.35f

The computational results support the presence of three lowenergy isomers of the reactants. These isomers could, in principle, all react to form products, however the results indicate that 4b_TS1 and 4c_TS1 are early transition states and correspond to the formation of the observed product with the strongest C-C bond.

In summary, we report the NMR detection of Pd^{IV} species fac-Pd(methyl)(p-tolyl)(alkynyl)(P-P)(OTf) that exhibit high selectivity for reductive elimination via tolyl-alkynyl coupling at low temperature. Kinetic studies indicate that elimination occurs directly from the six-coordinate complexes, with support from computational studies that also suggest that the preferred route is via the isomer with the alkynyl group trans to the triflate ligand, as illustrated in Scheme 1 for reagent 1 and R^1 = alkynyl.

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