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Synthesis and reactivity of extremely thermally stable trialkylpalladium(IV) complexes supported with 1,4,7-triazacyclononane

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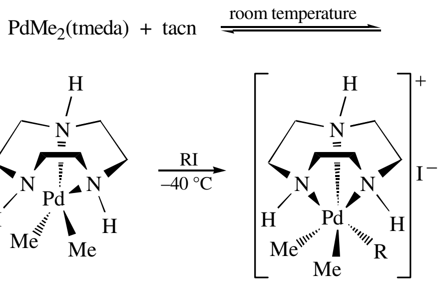
The dimethylpalladium(II) $PdMe_2$(tacn) complex supported with 1,4,7-triazacyclononane (tacn), obtained *in situ via* a reaction between $PdMe_2$(tmeda) and tacn reacts with methyl or ethyl iodide (RI) to form the most stable trialkyl palladium(IV) complexes [$PdMe_2$R(tacn)]I.

The chemistry of organopalladium(IV) compounds has been rapidly developed in the last two decades.[1] Being related to palladium(II)-mediated coupling reactions,[2] this chemistry is therefore of synthetic interest. In most cases, organopalladium(IV) species appear as unstable intermediates, and they cannot be fully characterised or isolated even when polydentate ligands are used to increase their stability.[3] This fact raises additional interest in these compounds, which can be good models for studying structure–reactivity relationships for organic transition metal complexes. Recent computational results in the oxidative addition–reductive elimination chemistry involving d^8–d^6 platinum metal complexes[4] allow one to design species to support d^6 metal complexes such as palladium(IV) coordination compounds or to find them among already known ligands. In particular, using model compounds, we found that 1,4,7-triazacyclononane can be more suitable for this role as compared with hydridotrispyrazolylborate or 1,4,7-trithiacyclononane.[4(*a*)] In this communication, we describe the synthesis and reactivity of new stable trialkylpalladium(IV) complexes supported with 1,4,7-triazacyclononane (tacn), [$PdMe_2$(R)(tacn)]$^+I^-$ (R = Me or Et). To the best of our knowledge, these are the most thermally stable complexes of this class.

New trialkylpalladium(IV) complexes were obtained as fine pale yellow powders in 50–60% yield by reacting one equivalent of iodomethane or iodoethane with an equimolar mixture of dimethyl(*N*,*N*,*N′*,*N′*-tetramethylethanediamine)palladium(II), $PdMe_2$(tmeda), and 1,4,7-triazacyclononane dissolved in deaerated dry acetone at –40 °C:



Since $PdMe_2$(tacn)[†] involved in the synthesis was obtained *in situ* in a fast reversible ligand exchange reaction, at room temperature (60% conversion under equilibrium conditions, acetone, 20 °C), iodoalkane behaved as a trapping reagent towards organopalladium(II) species. Thus, higher product yields can not be obtained. The new complexes are insoluble in water and poorly soluble in acetone or methanol, but they are readily soluble in DMSO. Other components of the equilibrated reaction mixture, $PdMe_2$(tmeda), *N*,*N*,*N′*,*N′*-tetramethylethanediamine and tacn, react with these iodoalkanes but with formation of compounds of higher solubility. Thus, the reaction product of iodomethane with $PdMe_2$(tmeda), the iodomethyl(*N*,*N*,*N′*,*N′*-tetramethylethanediamine)palladium(II) complex PdMeI(tmeda)[5] was isolated from the filtered reaction mixture after the addition of pentane at –10 °C and characterised by X-ray diffraction analysis.[6] Therefore, tmeda-supported palladium(IV) trialkyl complexes, which are presumably intermediates in a reaction between $PdMe_2$(tmeda) and the iodoalkanes, are short-lived.

The pure compound [$PdMe_3$(tacn)]$^+I^-$ was characterised by elemental analysis, ^1H and ^{13}C NMR spectroscopy and electrospray mass spectrometry.[‡] As compared with other trimethylpalladium(IV) compounds, this complex is extremely thermally stable, and it decomposes in the solid state at 152–154 °C. Ethane rather than methane is the sole hydrocarbon formed in the course of slow decomposition of [$PdMe_3$(tacn)]$^+I^-$ at 140 °C in a [$^2H_6$]DMSO solution.

$$[PdMe_3(tacn)]^+I^- \rightarrow C_2H_6 + PdMeI(tacn) \rightarrow \text{decomposition products}$$

The ethyldimethylpalladium(IV) derivative [$PdEtMe_2$(tacn)]$^+I^-$,[§] which is more stable than its trimethyl analogue, melts at 170 °C with decomposition. Its heating at 140 °C in a [$^2H_6$]DMSO solution for 4 h leads to the formation of propane as a major product, ethane and small amounts of ethene and methane (38 : 11 : 9 : 2 molar ratio according to NMR data). Whereas propane and ethane result from the reductive elimination of methyl and ethyl or two methyl ligands from the [$PdEtMe_2$(tacn)]$^+$ species, respectively, the accumulation of ethene may be due to hydride β-elimination from an iodoethylpalladium(II) complex, which is expected according to the reaction

$$[PdEtMe_2(tacn)]^+I^- \rightarrow \text{Me–Me} + PdEtI(tacn) \rightarrow CH_2{=}CH_2$$

This behaviour is similar to that of diorganopalladium(IV) intermediates, which exhibit much lower thermal stability. For example, the reaction of $PdMe_2$(tmeda) with ethyl iodide leads to the evolution of propane and ethane in a 3:2 ratio,[7] and the synthesised compounds can be used to model the chemistry of organopalladium(IV) intermediates.

Methane traces can be due to hydride β-elimination from [$PdEtMe_2$(tacn)]$^+$ and the subsequent decomposition of the unstable [$PdMe_2H$(tacn)]$^+$ species.

$$[PdEtMe_2(tacn)]^+I^- \rightarrow CH_2{=}CH_2 + [PdMe_2H(tacn)]^+I^- \rightarrow CH_4$$

All the known trialkylpalladium(IV) complexes supported with tridentate N-donor ligands can be decomposed at temperatures

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[†] *^1H NMR spectral data for* $C_8H_{21}N_3Pd$ at 300 MHz, δ: ([$^2H_6$]acetone) –0.43 (s, 6H, Pd–Me), 2.83 (m, 6H, N–CH_a), 3.19 (m, 6H, N–CH_b); (C_6D_6) 0.54 (s, 6H, Pd–Me), 2.23 (m, 6H, N–CH_a), 2.83 (m, 6H, N–CH_b); (CD_3CN) –0.43 (s, 6H, Pd–Me), 2.88 (m, 6H, N–CH_a), 3.20 (m, 6H, N–CH_b); ([$^2H_6$]DMSO) –0.43 (s, 6H, Pd–Me), 2.77 (m, 6H, N–CH_a), 3.09 (m, 6H, N–CH_b).

[‡] For $C_9H_{24}N_3IPd$: ^1H NMR (300 MHz, [$^2H_6$]DMSO) δ: 0.82 (s, 9H, Pd–Me), 2.78 (m, 6H, N–CH_a), 2.90 (m, 6H, N–CH_b), 5.22 (s, 3H, N–H). $^{13}C\{^1H\}$ NMR (500 MHz, [$^2H_6$]DMSO) δ: 9.66 (Me), 47.3 (CH_2). ES-MS, *m/z*: 280 [M]$^+$. Found (%): C, 27.21; H, 5.91; N, 10.26. Calc. for $C_9H_{24}N_3IPd$ (%): C, 26.52; H, 5.93; N, 10.31.

[§] For $C_{10}H_{26}N_3IPd$: ^1H NMR (300 MHz, [$^2H_6$]DMSO) δ: 0.81 (s, 6H, Pd–Me), 1.00 (t, 3H, C–Me, $^3J_{H–H}$ 7.6 Hz), 1.75 (q, 2H, Pd–CH_2, $^3J_{H–H}$ 7.6 Hz), 2.78 (m, 6H, N–CH_a), 2.92 (m, 6H, N–CH_b), 5.02 (s, 3H, N–H). $^{13}C\{^1H\}$ NMR (300 MHz, [$^2H_6$]DMSO) δ: 12.95 (Pd–Me), 17.57 (Pd–CH_2–*Me*), 26.36 (Pd–*C*H_2–Me), 47.50 (N–CH_2), 47.87 (N–CH_2), 48.04 (N–CH_2). Found (%): C, 28.72; H, 6.30; Pd, 25.20. Calc. for $C_{10}H_{26}N_3IPd$ (%): C, 28.48; H, 6.22; Pd, 25.24.

only slightly higher than room temperature.[3,5(*b*)] Other more thermally stable triorganopalladium(IV) compounds are a thio-analogue of the complex [$PdMe_3$(tacn)]I, derived from 1,4,7-trithiocyclononane (ttcn), [$PdMe_3$(ttcn)]I[8] and two neutral complexes supported with an anionic ligand, $PdMe_3[CpCo\{PR_2(O)\}_3]$ (R = OMe, OEt), which are decomposed at 117 °C (R = OMe) or 120 °C (R = OEt).[9]

Thus, the stability of cationic trialkylpalladium(IV) compounds can be increased with the help of facially chelating tridentate ligands, and quantum-chemical calculations can be used to trace trends in the effectiveness of the ligands.[4]

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