Synthesis of the Stable Organopalladium(IV) Complexes [*fac*-$PdRMe_2$(tripod)]X and Selective Reductive Elimination of Ethane from (η^1-Allyl)palladium(IV) Complexes To Form (η^3-Allyl)palladium(II) Complexes

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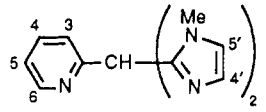
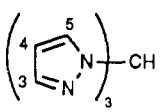
Oxidative addition of organo halides, RX, to dimethylpalladium(II) complexes, $PdMe_2$(tripod), has led to isolation of the first examples of ethyl-, *n*-propyl-, (η^1-benzyl)-, and (η^1-allyl)palladium(IV) complexes. With the tripod ligand as bis(1-methylimidazol-2-yl)(pyridin-2-yl)methane, (py)$(mim)_2$CH, the palladium(IV) complexes occur as mixtures of isomers with R trans to py and mim groups in [*fac*-$PdRMe_2${(py)-$(mim)_2$CH-*N*,*N*′,*N*″}]X. Tris(pyrazol-1-yl)methane as a ligand gives unstable palladium(IV) complexes, with the benzyl and 2-propenyl complexes undergoing facile reductive elimination of ethane to form organopalladium(II) products, including $[PdI(\eta^3\text{-}C_3H_5)]_2$ and the complex salt $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}]$-$[PdBr_2(\eta^3\text{-}C_3H_5)]$. Allyl exchange occurs for $[Pd(\eta^3\text{-}C_3H_5)(L)][PdBr_2(\eta^3\text{-}C_3H_5)]$ (L = $(pz)_3CH$, $(pz)_2CMe_2$), with $(pz)_3CH$ also exchanging coordinated and uncoordinated pz groups and with the cation $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]^+$ present as two conformers in equilibrium.

Introduction

Although organoplatinum(IV) complexes have been known since 1907,[1] organopalladium(IV) complexes were first isolated as pentafluorophenyl complexes in 1975[2] and as trimethylpalladium(IV) complexes in 1986.[3] For complexes containing the *fac*-$PdMe_3$ unit, tripodal nitrogen donor ligands give more stable complexes than related bidentate ligands; e.g., the tris(pyrazol-1-yl)methane complex [$PdMe_3\{(pz)_3CH\}$]I is stable at ambient temperature,[4,5]



(py)$(mim)_2$CH



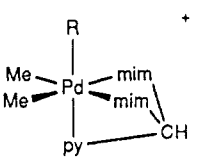
$(pz)_3$CH

but the 2,2′-bipyridyl complex $PdIMe_3$(bpy) requires storage at ca. −20 °C to avoid reductive elimination of ethane and formation of PdIMe(bpy).[3,5] In addition, for a series of cationic complexes formed by oxidative addition of iodomethane to $Pd^{II}Me_2$ complexes of tripod ligands, the complex containing bis(1-methylimidazol-1-yl)(pyridin-2-yl)methane, [$PdMe_3\{(py)(mim)_2CH\}$]I, is more stable than complexes of tripod ligands containing less basic pyrazol-1-yl groups.[5] Thus, to extend hydrocarbylpalladium(IV) chemistry beyond complexes containing the simple *fac*-$PdMe_3$ group, the complex $PdMe_2\{(py)$-$(mim)_2CH\}$ appears to be an ideal substrate for oxidative addition of organohalides. Ethyl, *n*-propyl, benzyl, and 2-propenyl halides have been chosen in order to probe the effect of the presence of β-hydrogens on the stability of palladium(IV) complexes and in recognition of the established importance of benzyl halides in the oxidative-addition chemistry of palladium substrates[6] and of the allyl group in palladium(I) and palladium(II) chemistry.[7] We report here the isolation of *fac*-$Pd^{IV}RMe_2$ complexes exhibiting structural isomerism for [$PdRMe_2\{(py)$-$(mim)_2CH\}$]X and the formation of $Pd^{II}(\eta^3\text{-}C_3H_5)$ species from reaction of $PdMe_2\{(pz)_3CH\}$ with 2-propenyl halides. A preliminary report of part of this work has appeared.[8]

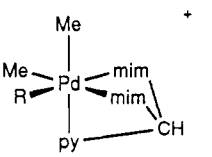
Results and Discussion

Complexes of (py)$(mim)_2$CH. ^{1}H NMR studies of the addition of EtI, Pr^nI, $PhCH_2Br$, C_3H_5I, and C_3H_5Br to $PdMe_2\{(py)(mim)_2CH\}$ in $(CD_3)_2CO$ at ambient temperature show the immediate formation of *fac*-$Pd^{IV}RMe_2$ complexes, and the complexes do not reductively eliminate on warming the solutions, indicating that isolation of complexes is feasible. The $Pd^{II}Me_2$ complex of the poor donor ligand pyridazine is an ideal substrate for the synthesis of $Pd^{II}Me_2$ and *fac*-$Pd^{IV}Me_3$ complexes,[9-11] and the $Pd^{IV}RMe_2$ complexes were isolated directly on addition of (py)$(mim)_2$CH to $[PdMe_2(pyd)]_n$ in acetone followed by addition of the organo halides and hexane.

The complexes exhibited poor to moderate solubility in $(CD_3)_2CO$ but were readily soluble in $CDCl_3$, in which they gave spectra showing the presence of two isomers, A and B, in ratios similar to that observed in $(CD_3)_2CO$ during addition of organo halides to $PdMe_2\{(py)(mim)_2CH\}$.



A



B

^{1}H NMR spectra are readily assigned from integration, multiplicities, and spin correlation spectroscopy (COSY); the relative intensities indicate A:B ratios of ca. 5:3 (R = Et), ca. 3:2 (Pr^n), ca. 1:1 (CH_2Ph), and ca. 6:5 (C_3H_5). Isomer A exhibits one PdR and one PdMe environment

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(2) Uson, R.; Fornies, J.; Navarro, R. *J. Organomet. Chem.* **1975**, *96*, 307; *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 235.
(3) Byers, P. K.; Canty, A. J.; Skelton, A. H.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1722.
(4) Byers, P. K.; Canty, A. J.; Skelton, A. H.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1093.
(5) Byers, P. K.; Canty, A. J.; Skelton, A. H.; White, A. H. *Organometallics*, **1990**, *9*, 826.
(6) For a recent review, see: Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, England, 1985; Vol. 2, p 625.
(7) See, e.g.: Maitlis, P. M.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 6, pp 265, 385.
(8) Byers, P. K.; Canty, A. J. *J. Chem. Soc., Chem. Commun.* **1988**, 639.
(9) Byers, P. K.; Canty, A. J.; Skelton, A. H.; White, A. H. *J. Organomet. Chem.* **1987**, *336*, C55.
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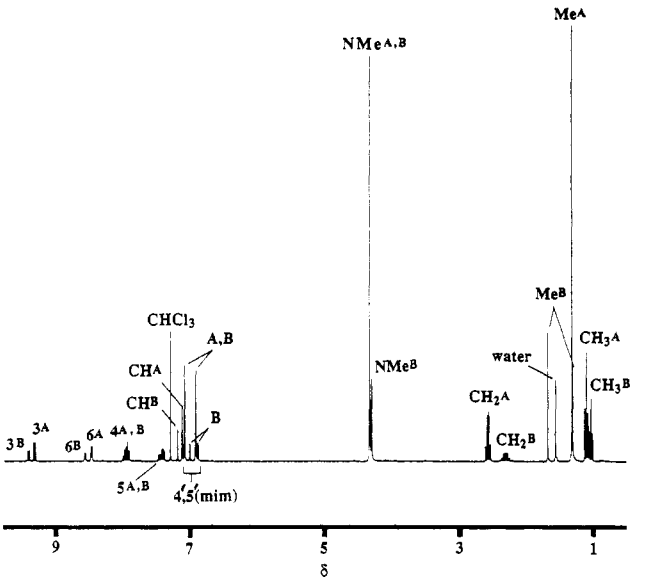


Figure 1. ^{1}H NMR spectrum of [*fac*-Pd(CH_2CH_3)Me_2{(py)-$(mim)_2CH$}]Br in $CDCl_3$, with assignment as isomer A or B indicated.

in the ratio 1:2 and one py and mim environment with the ratio 1:1 for $PdRMe_2$:(py)$(mim)_2CH$. Isomer B exhibits two PdMe and two mim environments, and the α-protons of the PdR group occur as complex resonances resulting from chirality at the palladium center. For example, isomer B for the *fac*-Pd(CH_2Ph)Me_2 complex exhibits two doublets for PdCH_2Ph compared with a singlet for isomer A, and the spectrum of [$PdEtMe_2${(py)$(mim)_2CH$}]Br is shown in Figure 1; the Pd(C_3H_5)Me_2 and *N*-Me region of the spectrum of [Pd(C_3H_5)Me_2{(py)$(mim)_2CH$}]Br is shown in the preliminary report of this work.[8]

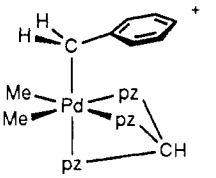
For the benzyl complex the pyridin-2-yl H6 resonance for isomer B (δ 7.74 dd) occurs ca. 0.7 ppm upfield from that for isomer A, consistent with anisotropic shielding by the benzyl group for B, an effect that is not possible for A since the benzyl group in A is trans to the py group.

The *fac*-Pd^{IV}(C_3H_5)Me_2 iodide and bromide complexes exhibit almost identical spectra, except that the ligand CH resonance is ca. 0.4 ppm more shielded in the iodide than in the bromide complex. A similar effect occurs for [$PdMe_3${(pz)$_3$CH}]X (X = I, BF_4), in which the ligand CH resonances differ by ca. 3.1 ppm and the H5(pz) resonances differ by ca. 0.45 ppm,[5] indicating that the cation···anion interaction occurs predominantly in this region of the cations.

The complexes of (py)$(mim)_2CH$ are the most stable organopalladium(IV) complexes isolated to date. No reductive elimination is detected on heating $(CD_3)_2CO$ solutions to ca. 60 °C, and the solid complexes are stable at ambient temperature.

Reaction of Alkyl Halides with $PdMe_2${(pz)$_3$CH}. Reactions were initially studied by ^{1}H NMR spectroscopy at 0 °C and at ambient temperature. *n*-Propyl iodide reacts slowly at ambient temperature with formation of a black precipitate (assumed to be Pd metal), and after ca. 1 h a resonance attributable to a trace of ethane is present. There is no evidence for the presence of Pd^{IV} species. Reaction with ethyl iodide gave complex spectra and formation of a black precipitate as the reaction progressed. Although the spectra are complex, resonances attributable to a Pd^{IV}$EtMe_2$ complex may be tentatively assigned as δ 2.65 (q, PdCH_2CH_3), 1.18 (t, ^3J = 7.6 Hz, $PdCH_2CH_3$), and 1.63 (s, PdMe). These resonances decrease in intensity with the appearance of resonances assigned to PdIMe{(pz)$_3$CH},[11] PdIEt{(pz)$_3$CH} (δ 0.89 t, ^3J = 7.3 Hz, $PdCH_2CH_3$; $PdCH_2CH_3$ obscured by EtI), ethylene (δ 5.38), ethane (δ 0.84), and methane (δ 0.17). The resonances attributed to the dissolved gases are identical with those for samples of the gases dissolved in $(CD_3)_2CO$.

Addition of benzyl bromide to $PdMe_2${(pz)$_3$CH} at 0 °C immediately gave a spectrum showing the presence of a Pd^{IV} complex, and after 12 h reaction was complete, only a trace of $PdMe_2${(pz)$_3$CH} and reductive-elimination products being present. The complex [Pd(CH_2Ph)Me_2-{(pz)$_3$CH}]Br was subsequently isolated; its ^{1}H NMR spectra revealed two pyrazole ring environments (in a 2:1 ratio) and singlets for the PdMe and $PdCH_2$ resonances:



An upfield shift of ca. 0.7 ppm is observed for the H3(pz) protons of the rings trans to PdMe, when compared with H3(pz) for the ring trans to $PdCH_2Ph$, consistent with orientation of the adjacent benzyl ring near these protons. A similar orientation away from the Pd^{IV}Me_2 group is shown in the X-ray structure of the 1,10-phenanthroline complex *fac*-PdBr(CH_2-*p*-C_6H_4Br)Me_2(phen).[12]

The spectrum of the BF_4 salt is very similar, except that its CH and H5(pz) resonances are, respectively, ca. 2.6 and 0.4 ppm more shielded than those of the bromide salt. The same trend has been observed for [$PdMe_3${(pz)$_3$CH}]X (X = I, BF_4).[5]

Although the complexes [Pd(CH_2Ph)Me_2{(pz)$_3$CH}]X (X = Br, BF_4) were isolated, they were insufficiently stable for outside microanalysis. The complex [Pd(CH_2Ph)-Me_2{(pz)$_3$CH}]Br was found to selectively reductively eliminate ethane at 25 °C in $(CD_3)_2CO$. The ^{1}H NMR spectra after ca. 1 h showed resonances attributable to ethane and PdBr(CH_2Ph){(pz)$_3$CH} only:

$$PdMe_2\{(pz)_3CH\} + PhCH_2Br \rightarrow [Pd(CH_2Ph)Me_2\{(pz)_3CH\}]Br \rightarrow PdBr(CH_2Ph)\{(pz)_3CH\} + Me\text{–}Me \quad (1)$$

The Pd^{II} complex exhibits variable-temperature spectra similar to those reported for PdIMe{(pz)$_3$CH}, with three broad pz resonances (H3,4,5) at ambient temperature resolved into nine resonances at −60 °C. A CH_2 singlet at ambient temperature for the $PdCH_2Ph$ protons is resolved into two doublets (4.26 and 2.68 ppm with J_{HH} = 6.0 Hz) at −60 °C, indicating that the benzyl group has a preferred conformation with inequivalent benzylic protons. The complex PdBr(CH_2Ph){(pz)$_3$CH} was isolated as an orange-yellow solid, but it could not be obtained in a pure form on recrystallization.

Reaction of Allyl Halides with $PdMe_2${(pz)$_3$CH}. Reaction of $PdMe_2${(pz)$_3$CH} with an excess of 2-propenyl iodide at ambient temperature in $(CD_3)_2CO$ is rapid, but the small amount of a Pd^{IV} species present in the first few minutes is completely absent after 10 min. At this time the NMR spectra show resonances of ethane, free (pz)$_3$CH, [PdI(η^3-C_3H_5)]$_2$, and a trace of PdIMe{(pz)$_3$CH}:

$$PdMe_2\{(pz)_3CH\} + C_3H_5I \rightarrow [Pd(\eta^1\text{-}C_3H_5)Me_2\{(pz)_3CH\}]I \rightarrow \tfrac{1}{2}[PdI(\eta^3\text{-}C_3H_5)]_2 + (pz)_3CH + Me\text{–}Me \quad (2)$$

The spectra indicate that selectivity for reductive elimi-

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nation to ethane and $[PdI(\eta^3\text{-}C_3H_5)]_2$ is almost quantitative, and in a preparative-scale reaction the allylpalladium(II) product was isolated in 90% yield; no palladium metal was formed.

The oxidative-addition and reductive-elimination reactions are much slower at −30 °C, and a spectrum obtained after 2 h at this temperature exhibits resonances for a Pd^{IV} cationic complex together with reductive-elimination products. Resonances attributed to the cation [*fac*-$Pd(CH_2CH{=}CH_{cis}H_{trans})Me_2\{(pz)_3CH\}]^+$ show two environments for the pyrazole rings, and there are also resonances at δ 1.47 (s, PdMe), 3.22 (d, $PdCH_2CH{=}CH_2$), and 5.11 (dd, $PdCH_2CH{=}CH_{cis}H$), both CH and CH_{trans} being partially hidden by resonances of unreacted 2-propenyl iodide.

Similar NMR studies of the reaction of 2-propenyl bromide with $PdMe_2\{(pz)_3CH\}$ allowed detection of [Pd-$(\eta^1\text{-}C_3H_5)Me_2\{(pz)_3CH\}]^+$ and reductive-elimination products. An (η^3-2-propenyl)palladium(II) complex, free $(pz)_3CH$, and ethane are formed, together with a trace of $PdBrMe\{(pz)_3CH\}$. Subsequent isolation and NMR characterization of the η^3-allyl complex, as a yellow crystalline solid of analytical composition "$Pd_2Br_2(allyl)_2\{(pz)_3CH\}$", showed it to be the complex salt $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}][PdBr_2(\eta^3\text{-}C_3H_5)]$:

$$PdMe_2\{(pz)_3CH\} + C_3H_5Br \rightarrow [Pd(\eta^1\text{-}C_3H_5)Me_2\{(pz)_3CH\}]Br \rightarrow \tfrac{1}{2}[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}][PdBr_2(\eta^3\text{-}C_3H_5)] + \tfrac{1}{2}(pz)_3CH + Me\text{-}Me \quad (3)$$

The complex salt is also obtained directly from reaction of $[PdBr(\eta^3\text{-}C_3H_5)]_2$ with $(pz)_3CH$ in acetone.

The spectrum of the salt in $(CD_3)_2CO$ at 25 °C exhibits resonances for one allyl and one $(pz)_3CH$ environment, but when the temperature is lowered to −60 °C, two allyl environments are indicated, one of which corresponds to the reported spectrum of $[PdBr_2(\eta^3\text{-}C_3H_5)]^-$.[13] Similar examples of allyl exchange have been reported, in particular for the tetramethylethylenediamine complex $[Pd(\eta^3\text{-}2\text{-butenyl})(tmeda)][PdCl_2(\eta^3\text{-}2\text{-butenyl})]$, and an X-ray structure has been reported for $[Pd(\eta^3\text{-}2\text{-propenyl})(tmeda)][PdCl_2(\eta^3\text{-}2\text{-propenyl})]$.[14] However, the $(pz)_3CH$ complex and a complex of a closely related bidentate ligand, 2,2-bis(pyrazol-1-yl)propane, exhibit additional exchange processes not shown by the tmeda complexes. The cation $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3CH\}]^+$ is expected to have $(pz)_3CH$ as a bidentate ligand with one uncoordinated pz ring, but the ^1H NMR spectrum at −60 °C exhibits one pz environment, indicating that the coordinated and uncoordinated rings exchange rapidly on the NMR time scale. Similar exchange occurs for $PdMe_2\{(pz)_3CH\}$.[11] An attempt to isolate the cation as a tetrafluoroborate salt by reaction with $AgBF_4$ failed, as the salt appeared to precipitate with AgBr and could not be recovered. However, synthesis of $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}][PdBr_2(\eta^3\text{-}C_3H_5)]$, from $PdMe_2\{(pz)_2CMe_2\}$ and C_3H_5Br (Pd^{IV} intermediate not detected), followed by reaction with $AgBF_4$ allowed isolation of $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]BF_4$ as a white crystalline solid. A comparison of low-temperature spectra confirms the presence of $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]^+$ in the complex salt and confirms the assignment of cation and anion resonances in the complex salt of $(pz)_3CH$.

In addition to the allyl group exchange between cation and anion, variable-temperature spectra of $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}][PdBr_2(\eta^3\text{-}C_3H_5)]$ indicate the occurrence of an additional exchange process. At low temperature two pz ring environments and four methyl group environments for the cation are seen for both the complex salt (Figure 2) and $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]BF_4$, consistent with the presence of two species in a ca. 5:3 ratio. Complexes of $(pz)_2CMe_2$ adopt a boat conformation for the chelate ring, e.g. as shown in the X-ray structural study of $PdCl_2\{(pz)_2CMe_2\}$,[15] and the complexes exhibit boat-to-boat ring inversion, e.g. for $PdX_2\{(pz)_2CMe_2\}$ (X = Cl,[15] Me[10]). The cation $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]^+$ is assumed to undergo similar behavior. The major isomer is tentatively assigned structure C, because molecular models indicate that D is expected to have greater allyl···CMe interactions.

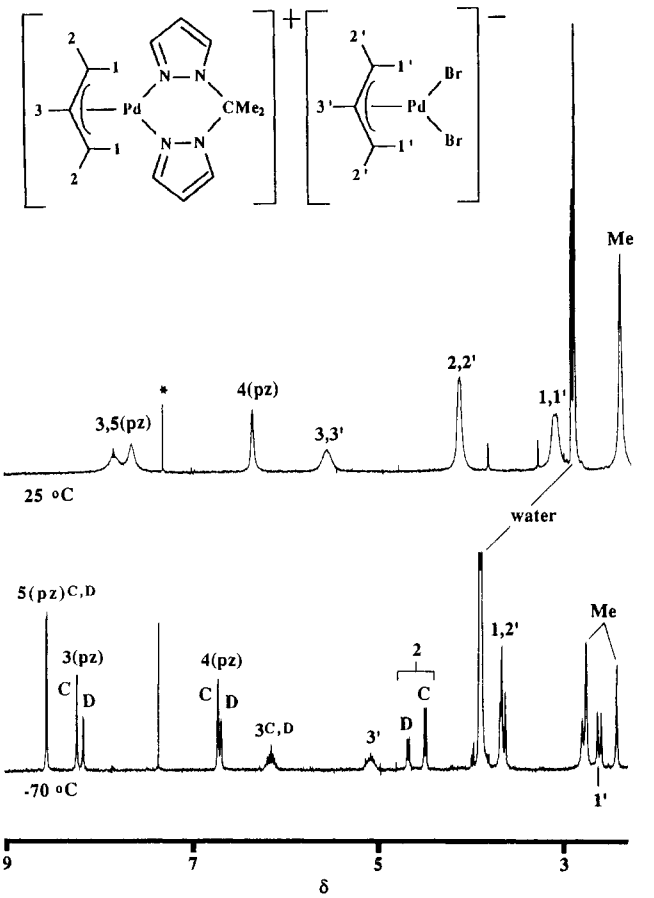
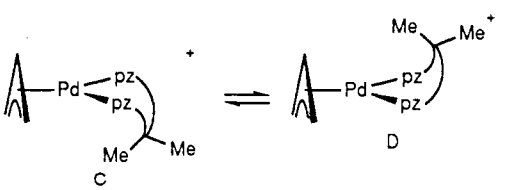


Figure 2. ^1H NMR spectra of $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}][PdBr_2(\eta^3\text{-}C_3H_5)]$ in $(CD_3)_2CO$ at +25 and −70 °C, illustrating η^3-propenyl resonances for the anion and cation and the presence of conformers C and D for the cation in a ca. 5:3 ratio. The methyl and H1 resonances for the cation are better resolved into four resonances in $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_2CMe_2\}]BF_4$. The asterisk indicates $CHCl_3$ impurity.



Concluding Remarks

The nitrogen donor $(py)(mim)_2CH$ has given the first examples of isolable ethyl-, propyl-, (η^1-benzyl)-, and (η^1-allyl)palladium(IV) complexes as the cations [*fac*-$PdRMe_2\{(py)(mim)_2CH\}]^+$, although preliminary accounts

(13) Goodfellow, R. J.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 784.
(14) Hegedus, L. S.; Akermark, B.; Olsen, D. J.; Anderson, O. P.; Zetterberg, K. *J. Am. Chem. Soc.* **1982**, *104*, 697.
(15) Minghetti, G.; Cinellu, M. A.; Bandini, A. L.; Banditelli, G.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *315*, 387.

of some neutral benzyl complexes have appeared, e.g. *fac*-$PdBr(CH_2Ph)Me_2(bpy)$,[8,12] and neutral 2-propenyl complexes have been isolated, e.g. *fac*-$PdI(C_3H_5)Me_2$-(phen).[16] The neutral benzyl complexes containing bpy and phen are stable in the solid state, but they are less stable than the cationic $(py)(mim)_2CH$ complexes in solution,[12] and the neutral 2-propenyl complexes reductively eliminate at ambient temperature in the solid state. The higher basicity of pyridine and 1-methylimidazole donor groups is assumed to account for the much higher stability of $(py)(mim)_2CH$ complexes compared with that of analogous $(pz)_3CH$ complexes, since stronger donor ligands are expected to enhance the stability of higher oxidation states and are established as a general factor in reducing the tendency toward reductive elimination from related d^8 complexes.[17]

Allylpalladium(II) complexes,[18] including nitrogen donor complexes,[19] have important applications in organic synthesis, and there are indications that allyl halides promote reductive elimination from $Pd(\eta^3\text{-allyl})(aryl)(PPh_3)$ via oxidative addition to form Pd^{IV} intermediate(s).[20] The isolation of stable allylpalladium(IV) complexes of nitrogen donor ligands and the selectivity of the coupling of methyl groups to form ethane from Pd^{IV} complexes of the readily available poly(pyrazol-1-yl)alkane ligands provide interesting model compounds and reactions to assist with further studies of mechanisms of organic synthesis using allylpalladium(II) complexes.

The results reported here indicate the potential for development of an extensive organometallic chemistry of palladium(IV) beyond the initial reports of (pentafluorophenyl)- and trimethylpalladium(IV) chemistry.

Experimental Section

The reagents $(pz)_2CMe_2$,[21] $(pz)_3CH$, $(py)(mim)_2CH$, $PdMe_2(L)$ (L = $(pz)_3CH$, $(py)(mim)_2CH$),[11] and $[PdMe_2(pyd)]_n$ and $PdMe_2[(pz)_2CMe_2]$[10] were prepared as described, and both solvents and organo halide reagents were dried and distilled. All new complexes were dried under high vacuum. Microanalyses were performed by the Canadian Microanalytical Service, Vancouver, Canada. ^1H NMR spectra were recorded with a Bruker AM 300 spectrometer, chemical shifts being given in ppm relative to Me_4Si. Studies of the reactivity of $Pd^{II}Me_2$ complexes toward organo halides were carried out as described for $PdMe_2(L_2)$ (L_2 = bpy, phen).[5]

Synthesis of Complexes. [*fac*-PdEtMe$_2$\{(py)(mim)$_2$CH\}]I. Bis(1-methylimidazol-2-yl)(pyridin-2-yl)methane (0.35 g, 1.39 mmol) was added to a suspension of dimethyl(pyridazine)palladium(II) (0.30 g, 1.39 mmol) in acetone (30 mL) at 0 °C. The mixture was stirred for 1–2 min and filtered into a precooled round-bottomed flask. Addition of iodoethane (0.5 mL, 6.2 mmol), followed by rotary evaporation to half volume at 0 °C, addition of cold hexane (10 mL), and further evaporation, gave the complex. The white solid was collected and washed with cold diethyl ether (73% yield). ^1H NMR ($CDCl_3$; see Figure 1, δ): mim trans to PdMe for both isomers, 7.06 (d, H4′ or 5′) and 6.88 (d, J_{45} = 1.4 Hz, H5′ or 4′), 4.32 (s, 1-Me); isomer A py trans to PdEt, 9.30 (d, J_{34} = 7.8 Hz, H3), 8.45 (dd, J_{56} = 5.6 Hz, J_{46} = 1.5 Hz, H6), 7.91 (m, H4), 7.37 (ddd, J_{45} = 7.6, J_{56} = 5.3, J_{35} = 1.3 Hz, H5) 7.10 (s, CH), 2.56 (q, ^3J = 7.5 Hz, $PdCH_2$), 1.30 (s, PdMe trans to mim), 1.09 (t, ^3J = 7.5 Hz, $PdCH_2CH_3$); isomer B, mim trans to PdEt, 6.98 (d, H4′ or 5′) and 6.86 (d, J_{45} = 1.2 Hz, H5′ or 4′), 4.29 (s, 1-Me), py trans to PdMe, 9.39 (d, J_{34} = 7.8 Hz, H3), 8.54 (m, J_{56} = 5.3 Hz, H6), 7.96 (m, H4), 7.44 (m, H5), 7.17 (s, CH), 2.28 (m, $PdCH_2$ trans to mim), 1.55 (s, PdMe trans to py), 1.29 (s, PdMe trans to mim), 1.02 (t, ^3J = 7.6 Hz, $PdCH_2CH_3$ trans to mim). Isomers A and B are in a ca. 5:3 ratio. Anal. Calcd for $C_{19}H_{25}N_4IPd$: C, 39.6; H, 4.8; N, 12.8. Found: C, 39.6; H, 4.7; N, 12.7.

The complexes [*fac*-$PdRMe_2$\{(py)(mim)$_2$CH\}]X (RX = $PhCH_2Br$, CH_2CHCH_2Br, CH_2CHCH_2I) were obtained by an identical procedure.

[*fac*-Pd(CH$_2$Ph)Me$_2$\{(py)(mim)$_2$CH\}]Br; yield 58%. ^1H NMR ($CDCl_3$, δ): isomers A and B, 7.47 (s) and 7.38 (s, CH), 7.2–6.8 (m, Ph); isomer A, mim trans to PdMe, 6.71 (d, H4′ or 5′) and 6.33 (d, J_{45} = 1.4 Hz, H5′ or 4′), 4.30 (s, 1-Me), py trans to $PdCH_2Ph$, 9.34 (m, H3), 8.42 (dd, J_{56} = 5.4, J_{46} = 1.3 Hz, H6), 7.90 (ddd, $J_{45} \approx J_{34} \approx 7.7$, J_{46} = 1.6 Hz, H4), 7.36 (m, H5), 3.67 (s, $PdCH_2Ph$), 1.46 (s, PdMe trans to mim); isomer B, mim, 6.95 (d) and 6.83 (d) and 6.78 (d) and 6.53 (d, J_{45} = 1.4 Hz, H4′ and H5′), 4.36 (s) and 4.27 (s, 1-Me), py trans to PdMe, 9.37 (m, H3), 7.82 (ddd, $J_{45} \approx J_{34} \approx 7.7$, $J_{46} \approx 1.7$ Hz, H4), 7.74 (dd, J_{56} = 5.4, J_{46} = 1.3 Hz, H6), 7.09 (m, H5), 3.57 (d) and 3.29 (d, J_{HH} = 8.4 Hz, $PdCH_2Ph$), 1.66 (s, PdMe trans to py), 1.44 (s, PdMe trans to mim). Isomers A and B are in a ca. 1:1 ratio. Anal. Calcd for $C_{24}H_{27}N_4BrPd$: C, 49.3; H, 5.0; N, 12.5. Found: C, 49.5; H, 4.9; N, 12.2.

[*fac*-Pd(CH$_2$CH=CH$_2$)Me$_2$\{(py)(mim)$_2$CH\}]Br; yield 76%. ^1H NMR ($CDCl_3$, δ): isomers A and B, 6.88 (d, J_{45} = 1.5 Hz, H5 or 4), 5.84 (m, $PdCH_2CHCH_2$), 5.25 (m, $PdCH_2CHCHH$ trans to CH), 5.07 (m, $PdCH_2CHCHH$ cis to CH); isomer A, mim trans to PdMe, 7.07 (d, H4′ or 5′), 4.37 (s, 1-Me), py trans to allyl, 9.45 (m, H3), 8.45 (dd, J_{56} = 5.5, J_{46} = 1.4 Hz, H6), ~7.94 (m, H4), ~7.38 (m, H5), 7.53 (s, CH), 3.16 (d, ^3J = 8.2 Hz, $PdCH_2CHCH_2$ trans to py), 1.40 (s, PdMe trans to mim); isomer B, mim, 7.09 (d) and 6.99 (d) and 6.86 (d, J_{45} = 1.4 Hz, H4′,5′), 4.38 (s) and 4.35 (s, 1-Me), py trans to PdMe, 9.47 (m, H3), 8.55 (dd, J_{56} = 5.1, J_{46} = 1.3 Hz, H6), 7.97 (m, H4), 7.42 (m, H5), 7.59 (s, CH), 2.93 (m, $PdCH_2CHCH_2$ trans to mim), 1.62 (s, PdMe trans to py), 1.38 (s, PdMe trans to mim). Isomers A and B are in a ca. 6:5 ratio. Anal. Calcd for $C_{20}H_{25}N_4BrPd$: C, 44.7; H, 5.1; N, 13.7. Found: C, 44.4; H, 5.0; N, 13.6.

[*fac*-Pd(CH$_2$CH=CH$_2$)Me$_2$\{(py)(mim)$_2$CH\}]I; yield 19%. ^1H NMR ($CDCl_3$, δ): isomers A and B, 7.94 (m, H4(py)), 7.40 (m, H5(py)), 6.88 (m, H5′ or 4′, mim trans to PdMe (A), mim (B)), 5.81 (m, $PdCH_2CHCH_2$), 5.24 (m, $PdCH_2CHCHH$ trans to CH), 5.06 (m, $PdCH_2CHCHH$ cis to CH); isomer A, mim trans to PdMe, 7.06 (d, J_{45} = 1.5 Hz, H4′ or 5′), 4.31 (s, 1-Me), py trans to allyl, 9.32 (d, J_{34} = 7.6 Hz, H3), 8.44 (dd, J_{56} = 5.2 Hz, H6), 7.19 (s, CH), 3.14 (dd, ^3H = 8.5 Hz, $PdCH_2CHCH_2$ trans to py), 1.38 (s, PdMe trans to mim); isomer B, mim, 7.09 (d) and 6.99 (m) and 6.86 (d, H4′,5′), 4.39 (s) and 4.32 (s, 1-Me), py trans to PdMe, 9.36 (d, J_{34} = 7.6 Hz, H3), 8.54 (dd, J_{56} = 5.2 Hz, H6), 7.25 (s, CH), 2.91 (m, $PdCH_2CHCH_2$ trans to mim), 1.61 (s, PdMe trans to py), 1.36 (s, PdMe trans to mim). Isomers A and B are in a ca. 1:1 ratio. Anal. Calcd for $C_{20}H_{25}N_4IPd$: C, 41.2; H, 4.5; N, 12.7. Found: C, 41.3; H, 4.6; N, 12.7.

[*fac*-PdPr^{n}Me$_2$\{(py)(mim)$_2$CH\}]I. A similar procedure was followed, but with removal of all acetone by rotary evaporation to give a viscous red oil, followed by addition of a small amount of acetone to give a cream crystalline solid (42% yield). ^1H NMR ($CDCl_3$, δ): isomers A and B, 6.88 (m, H5′ or 4′, mim trans to PdMe), ~1.52 (m, $PdCH_2CH_2CH_3$ trans to py), 0.91 (m, $PdCH_2CH_2CH_3$ (trans to py (A), trans to mim (B)); isomer A, mim trans to PdMe, 7.06 (d, J_{45} = 1.5 Hz, H4′ or 5′), 4.31 (s, 1-Me), py trans to Pr^n, 9.31 (d, J_{34} = 7.7 Hz, H3), 8.45 (d, J_{56} = 5.2 Hz, H6), 7.91 (m, H4), 7.38 (m, H5), 7.12 (s, CH), 2.42 (m, $PdCH_2$ trans to py), 1.31 (s, PdMe trans to mim); isomer B, mim trans to PdMe, 7.02 (d, J_{45} = 1.4 Hz, H4′ or 5′), 4.32 (s, 1-Me), mim trans to PdPr^n, 7.00 (d, H4′ or 5′) and 6.85 (d, J_{45} = 1.2 Hz, H5′ or 4′), 4.28 (s, 1-Me), py trans to PdMe, 9.39 (d, J_{34} = 7.5 Hz, H3), 8.54 (d, J_{56} = 5.2 Hz, H6), 7.96 (m, H4), 7.42 (m, H5), 7.18 (s, CH), 2.17 (m, $PdCH_2$ trans to mim), 1.55 (s, PdMe trans to py), 1.30 (s, PdMe trans to mim). Isomers A and B are in a ca. 3:2 ratio. Anal. Calcd for $C_{20}H_{27}N_4IPd$: C, 41.1; H, 4.9; N, 12.6. Found: C, 41.0; H, 4.9; N, 12.6.

[*fac*-Pd(CH$_2$Ph)Me$_2$\{(pz)$_3$CH\}]Br. Benzyl bromide (0.2 mL, 1.69 mmol) was added to a solution of $PdMe_2[(pz)_3CH]$ (0.4 g, 1.14

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mmol) in acetone (20 mL) at 0 °C. The solution was stirred for 70 min at 0 °C, followed by rotary evaporation to ca. 10 mL at 0 °C and addition of cold hexane. When the solution was cooled to ca. −20 °C for 1 h, the product formed as a cream crystalline solid (49%). ^{1}H NMR ($CDCl_3$, δ): 12.07 (s, 1, CH), 8.90 (d, 2, J_{45} = 2.4 Hz, H5, pz trans to PdMe), 8.82 (d, 1, J_{45} = 2.3 Hz, H5, pz trans to $PdCH_2Ph$), 7.63 (d, 1, J_{34} = 2.1 Hz, H3, pz trans to $PdCH_2Ph$), 7.15 (m, 1, H4, Ph), 7.04 (t, 2, ^3J = 7.5 Hz, H3,5, Ph), 6.96 (m, 4, H3, pz trans to PdMe, and H2,6, Ph), 6.40 ("t", 1, H4, pz trans to $PdCH_2Ph$), 6.28 ("t", 2, H4, pz trans to PdMe), 3.62 (s, CH_2), 1.71 (s, PdMe).

[*fac*-Pd(CH$_2$Ph)Me$_2${(pz)$_3$CH}]BF$_4$. Addition of silver tetrafluoroborate (0.4 mmol) in acetone to a stirred solution of [Pd(CH$_2$Ph)Me$_2${(pz)$_3$CH}]Br (0.2 g, 0.38 mmol) in acetone at 0 °C resulted in the immediate precipitation of AgBr. Filtration, followed by addition of hexane at 0 °C, gave the product as a white crystalline solid, which was isolated by filtration and washed with hexane (89%). ^{1}H NMR ($CDCl_3$, δ): 9.48 (s, 1, CH), 8.43 (m, 3, H5, pz), 7.66 (d, 1, J_{34} = 2.1 Hz, H3, pz trans to $PdCH_2Ph$), 7.17 (m, 1, H4, Ph), 7.05 (m, 2, H3,5, Ph), 6.96 (m, 3, H3, pz trans to PdMe, and H2,6, Ph), 6.43 ("t", 1, H4, pz trans to $PdCH_2Ph$), 6.31 (m, 2, H4, pz trans to PdMe), 3.62 (s, CH_2), 1.72 (s, PdMe).

[Pd(η^3-C$_3$H$_5$){(pz)$_3$CH}][Pd(η^3-C$_3$H$_5$)Br$_2$]. 2-Propenyl bromide (0.06 mL, 0.69 mmol) was added to a solution of PdMe$_2${(pz)$_3$CH} (0.20 g, 0.57 mmol) in acetone, and the solution was stirred for 60 min. Addition of hexane and slow evaporation of acetone under reduced pressure at 0 °C gave the product as a dark yellow crystalline solid, which was isolated by filtration and washed with hexane (39%). ^{1}H NMR ($(CD_3)_2CO$, δ): at 25 °C, 9.26 (s(b), 1, CH), 8.07 (d(b), 3, H5), 7.75 (d(b), 3, H3, pz), 6.47 ("t"(b), 4, H4), 5.56 (m(b), 2, H3), 4.11 (d(b), 4, H2), 3.17 (d(b), 4, H1); at −60 °C, cation, 10.04 (s(b), 1, CH), 8.79 (d(b), 3, H5, pz), 8.13 (d(b), 3, H3, pz), 6.66 (s(b), 3, H4, pz), 6.04 (m, 1, H3), 4.46 (d, J_{23} = 6.5 Hz, 2, H2), 3.37 (d, J_{13} = 12.0 Hz, 2, H1), anion, 5.33 (m, 1, H3′), 3.85 (d, J_{23} = 6.8 Hz, 2, H2′), 2.81 (d, J_{13} = 12.1 Hz, 2, H1′). Anal. Calcd for $C_{16}H_{20}N_6Br_2Pd$: C, 28.7; H, 3.0; N, 12.6. Found: C, 29.1; H, 3.0; N, 12.5.

An identical procedure employing 2-propenyl iodide gave [Pd(η^3-C$_3$H$_5$)I]$_2$ in 90% yield. The ^{1}H NMR spectrum ($CDCl_3$) is identical with that reported.[22]

[Pd(η^3-C$_3$H$_5$){(pz)$_2$CMe$_2$}][Pd(η^3-C$_3$H$_5$)Br$_2$]. A similar procedure gave this complex in 63% yield. ^{1}H NMR ($(CD_3)_2CO$; see Figure 2; δ): at 25 °C all resonances are broad and definite assignments have not been attempted, 7.89, 7.70, 6.38, 5.58, 4.14, 3.10, 2.40; at −60 °C, 3.69–3.63 (m, H1, cation, and H2′, anion), cation, conformers C and D, 8.59 (d, J_{45} = 2.8 Hz, H5, pz), 6.16 (m, H3), 2.80 (s) and 2.76 (s) and 2.42 (s, Me), conformer A, 8.26 (d, J_{34} = 1.9 Hz, H3, pz), 6.73 ("t", H4, pz), 4.49 (d, J_{23} = 6.7 Hz, H2), conformer B, 8.20 (s, H3, pz), 6.70 ("t", H4, pz), 4.68 (d, J_{23} = 6.7 Hz, H2), anion, 5.06 (m, H3′), ~3.81 (m, H2′), 2.62 (d, J_{13} = 12.0 Hz, H1′). Anal. Calcd for $C_{15}H_{22}N_4Br_2Pd$: C, 28.6; H, 3.5; N, 8.9. Found: C, 28.8; H, 3.5; N, 8.9.

[Pd(η^3-C$_3$H$_5$){(pz)$_2$CMe$_2$}]BF$_4$. A procedure similar to that for the synthesis of [Pd(CH$_2$Ph)Me$_2${(pz)$_3$CH}]BF$_4$ gave the complex as a white crystalline solid (22%). ^{1}H NMR ($(CD_3)_2CO$, δ): at 25 °C, 8.43 (d, J_{45} = 2.8 Hz, 2, H5, pz), 8.10 (d, J_{45} = 1.8 Hz, 2, H3, pz), 6.63 (dd, J_{34} = 1.7, J_{45} = 2.8 Hz, 2, H4, pz), 6.12 (m, 1, H3), 4.56 (d, J_{23} = 7.0 Hz, 2, H2), 3.63 (d, J_{13} = 12.4 Hz, 2, H1), 2.74, 2.56 (s, 6, Me); At −70 °C, conformers C and D, 8.56 (d, J_{45} = 2.4 Hz, H5, pz), 6.14 (m, H3), conformer C, 8.26 (d, J_{34} = 2.0 Hz, H3, pz), 6.75 ("t", H4, pz), 4.50 (d, J_{23} = 6.8 Hz, H2), 3.60 (d, J_{13} = 12.5 Hz, H1), 2.73 (s) and 2.42 (s, Me), conformer D, 8.17 (d, J_{34} = 2.0 Hz, H3, pz), 6.71 ("t", H4, pz), 4.67 (d, J_{23} = 6.9 Hz, H2), 3.66 (d, J_{13} = 12.5 Hz, H1), 2.77 (s) and 2.75 (s, Me). Anal. Calcd for $C_{12}H_{17}N_4BF_4Pd$: C, 35.1; H, 4.2; N, 13.6. Found: C, 35.0; H, 4.1; N, 13.4.

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Pressure and Solvent Dependence of the Substitution Behavior of Octahedral Metal Carbonyl Complexes: Influence of Electronic Effects on Reaction Mechanism

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The kinetics of the substitution reaction M(phen)(CO)$_4$ + P ⇌ *fac*-M(phen)(CO)$_3$P + CO (phen = 1,10-phenanthroline, P = P(OMe)$_3$) has been studied in six different solvents for M = Mo at 50 °C. The pressure dependence of the forward reaction was studied in 1,2-dichloroethane (M = Mo, Cr) and in toluene (M = Mo). In addition, the reverse reaction of Cr(phen)(CO)$_3$P with CO in dichloroethane was studied as a function of pressure, and the partial molar volumes of all species were determined. For molybdenum, a two-term rate law, rate = (k_i + k_L [P])[complex], was observed in each case, while for chromium a complex rate law gave limiting rate constants at zero and high phosphite concentrations. The rate constants of the k_i pathway in the six solvents are correlated with the MLCT band energies and discussed in terms of transition-state stabilization. The volumes of activation (M = Mo: $\Delta V^{\ddagger}_{k_i}$ = +8.4 ± 0.7 and +2 ± 2 cm^3·mol^{-1} and $\Delta V^{\ddagger}_{k_L}$ = −21 ± 2 and −13 ± 1 cm^3·mol^{-1} for CO-saturated dichloroethane and toluene, respectively; M = Cr: $\Delta V^{\ddagger}$ = +13.8 ± 0.5 and +19.2 ± 0.5 cm^3·mol^{-1} for the forward and reverse reactions, respectively) are in full agreement with the proposed scheme of parallel associative and dissociative reversible reactions. The reaction volume obtained from the volume profile for the substitution of Cr(phen)(CO)$_4$ by P(OMe)$_3$ (−4 ± 1 cm^3·mol^{-1}) is in good agreement with that calculated from the kinetic data (−5.4 ± 0.5 cm^3·mol^{-1}).

Introduction

Both square-planar and octahedral complexes undergo under certain circumstances substitution according to a two-term rate law:[1-3]

$$\text{rate} = (k_i + k_L[\text{nucleophile}])[\text{complex}] \quad (1)$$

The controversy over the dissociative or associative nature of the intimate mechanism (here represented by the k_i

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