# Heterobimetallic Templates for Carbon–Carbon Bond Formation by Migratory Insertion Reactions involving CO, Isonitriles or Olefins

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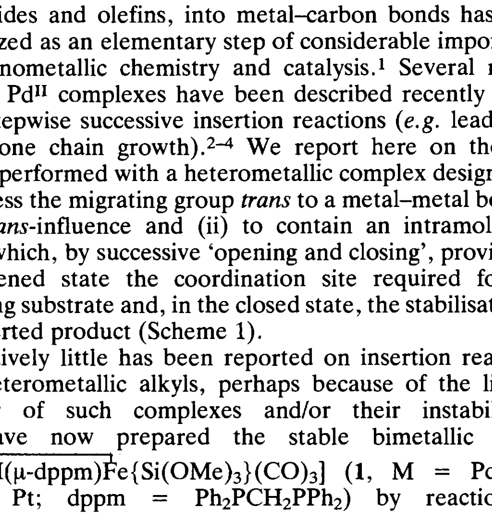
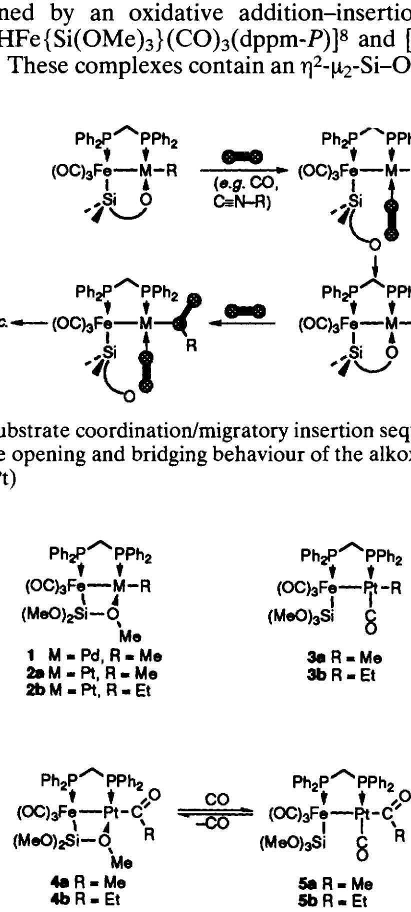
New patterns for heterobimetallic reactivity are presented that combine electronic effects (of the metal–metal bond) and steric control (by a bridging, hemilabile trialkoxysilyl ligand) in organometallic insertion reactions involving isonitriles, CO and olefins.

The insertion of small molecules, such as CO, organic isocyanides and olefins, into metal–carbon bonds has been recognized as an elementary step of considerable importance in organometallic chemistry and catalysis.[1] Several mononuclear $Pd^{II}$ complexes have been described recently which allow stepwise successive insertion reactions (*e.g.* leading to polyketone chain growth).[2–4] We report here on the first studies performed with a heterometallic complex designed (i) to possess the migrating group *trans* to a metal–metal bond of high *trans*-influence and (ii) to contain an intramolecular donor which, by successive 'opening and closing', provides in the opened state the coordination site required for the incoming substrate and, in the closed state, the stabilisation of the inserted product (Scheme 1).

Relatively little has been reported on insertion reactions with heterometallic alkyls, perhaps because of the limited number of such complexes and/or their instability.[5,6] We have now prepared the stable bimetallic alkyls $[(Me)\overline{M(\mu\text{-dppm})Fe}\{Si(OMe)_3\}(CO)_3]$ (**1**, M = Pd; **2a**, M = Pt; dppm = $Ph_2PCH_2PPh_2$) by reaction of $[M(Me)Cl(1,5\text{-cod})]$[7] with $[Fe\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]^-$ in THF, whereas $[(Et)\overline{Pt(\mu\text{-dppm})Fe}\{Si(OMe)_3\}(CO)_3]$ **2b** was obtained by an oxidative addition–insertion reaction between $[HFe\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]$[8] and $[Pt(C_2H_4)_3]$ in toluene. These complexes contain an $\eta^2$-$\mu_2$-Si–O bridge ($^1H$ and $^{31}P\{^1H\}$ NMR evidence) that is dynamic on the $^1H$ NMR time scale in the case of palladium, the exchange between the OMe groups resulting most likely from rapid rotation of the $-Si(OMe)_3$ ligand about the Fe–Si bond.[9] The donor interaction SiO → Pt in complexes **2** is displaced by CO ($CH_2Cl_2$, 20 °C) to give **3** in which this ligand occupies the suitable *cis* position with respect to the alkyl group. These complexes represent rare examples in which a CO and an alkyl ligand bound *cis* to each other in a square planar environment have been observed under ambient conditions.[7a,10a,c] However, after *ca.* 30 min, acyl formation has occurred which liberates a coordination site and the dative O → Pt intramolecular interaction is restored, resulting in complexes **4**. The latter bind CO reversibly, since bubbling of CO through their $CH_2Cl_2$ solution quantitatively affords **5**, which lose their terminal Pt-bound CO on purging (but not the acyl CO) (Scheme 2). All the successive 'opening and closing' steps involving the trialkoxysilyl ligand may thus be easily identified in the Fe–Pt systems. They will also form the basis for the behaviour of analogous Fe–Pd complexes, although the much higher reactivity of the latter has precluded characterization of all the individual steps.

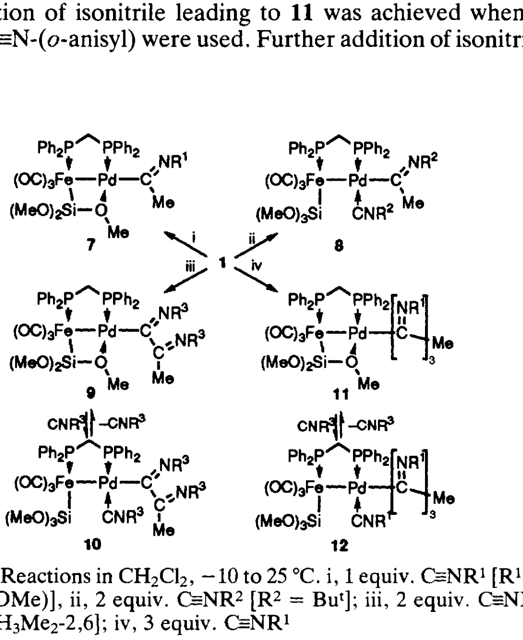


**Scheme 1** Substrate coordination/migratory insertion sequence resulting from the opening and bridging behaviour of the alkoxysilyl ligand (M = Pd, Pt)

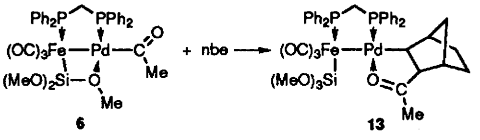


**Scheme 2**

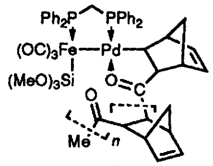
Under a CO atmosphere, the bimetallic alkyl **1** in $CH_2Cl_2$ afforded within 1 h the acyl complex **6** in good yields. In contrast to most palladium acyl complexes, **6** is stable with respect to CO de-insertion. Reaction of **1** with 1 equiv. C≡N-(*o*-anisyl) yielded the imino acyl complex **7**, analogous to **6** (Scheme 3). Reaction with two equivalents C≡N-$Bu^t$ selectively gave **8**, whereas with the more reactive C≡N-(2,6-xylyl), bis-insertion occurred readily to give **9** selectively. In the presence of excess C≡N-(2,6-xylyl), an equilibrium was established with **10** which contains a Pd-bound terminal isonitrile [ν(CN) = 2173 $cm^{-1}$] in place of the dative O → Pd bond. The reaction of **1** with two equiv. C≡N-(*o*-anisyl) gave a mixture of mono-, di- and tri-insertion products. Selective tri-insertion of isonitrile leading to **11** was achieved when 3 equiv. C≡N-(*o*-anisyl) were used. Further addition of isonitrile



**Scheme 3** Reactions in $CH_2Cl_2$, −10 to 25 °C. i, 1 equiv. C≡$NR^1$ [$R^1$ = $C_6H_4$ (*o*-OMe)], ii, 2 equiv. C≡$NR^2$ [$R^2$ = $Bu^t$]; iii, 2 equiv. C≡$NR^3$ [$R^3$ = $C_6H_3Me_2$-2,6]; iv, 3 equiv. C≡$NR^1$



Scheme 4



**14**

opens again the dative O → Pd interaction to give **12** [ν(CN) = 2186 $cm^{-1}$], en route to the next migratory insertion.[11]

Olefin insertion into the Pd-acyl bond of **6** occurred quantitatively after 3 h in the presence of norbornene (nbe) to give **13** whose $^1H$ NMR data indicate that *cis* addition of Pd–C(O)Me across the exo face of norbornene has occurred (Scheme 4). The IR data confirm the expected coordination of the acyl group to palladium, resulting in a five-membered chelate rather than the less favoured Fe–Si–O → Pd four-membered ring.[12,13]

Further CO insertion into the newly formed Pd–C bond of the norbornadiene (nbd) analogue of **13** took place under a CO atmosphere and this reaction was accelerated in the presence of excess nbd. It led to stable **14** which contains an oligomeric chain with alternating CO and nbe units whose exact length is not known at the moment (mononuclear complexes related to **14** with *n* = 1–3 have been characterized by IR, $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR).[10b] This indicates that olefin insertion into the Pd–acyl bond is more facile than CO insertion into a Pd–alkyl bond. No olefin insertion was observed in the case of the platinum complex **4a** (ethylene or nbd, $CH_2Cl_2$, 20 °C).

The mechanism of these insertion reactions obeys the following pattern: opening of the labile SiO → Pd bond, coordination of the substrate, *cis* migration, isomerization and closing of the Fe–Si–O → Pd ring. The unique behaviour of the -Si(OMe)$_3$ ligand in these systems extends to bimetallic chemistry the concept of hemilabile or 'dangling' chelating ligands, which has been successfully used in mononuclear chemistry.[14] The bimetallic nature of all the complexes presented here is readily ascertained in solution by $^{31}P\{^1H\}$ NMR where an AX pattern is always observed. The $^{2+3}J(PP)$ values are diagnostic for the presence or absence of an $\eta^2$-μ-Si–O bridge: in the former case, this coupling constant is *ca.* 40 Hz smaller than in the latter. Although pentacoordinated intermediates have not been detected and need not be invoked in this mechanism, their involvement in the course of the displacement of the O → M bond cannot be excluded.

The favourable conditions for (i) *cis* coordination of the entering substrate and (ii) *cis* migration of the alkyl group are built in the design of our bimetallic system since (i) the thermodynamically preferred *trans*-P–Fe–Si arrangement forces the labile, dative SiO → M bond to be *cis* to the M–R bond and (ii) the high *trans* influence of the metal–metal bond, which is always *trans* to the M–R bond, promotes migration of the R group. These features emphasize the interesting chemo- and stereochemical control resulting from the appropriate interplay between metal–metal and metal–ligand interactions in heterometallic systems.

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## Footnote

† Selected NMR spectroscopic data at 298 K. $^{31}P\{^1H\}$ NMR (121.5 MHz) spectra were referenced to external $H_3PO_4$. J values given in Hz. Complex **1**, $^1H$ NMR (300 MHz, $C_6D_6$): δ 0.82 (s, 3H, PdMe), 3.49 [t, 2H, $PCH_2P$, $^2J(PH)$ 10.1], 3.91 (s, vbr, 9H, OMe); $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ 42.2 [d, $^{2+3}J(PP)$ 51, P(Pd)], 63.5 [d, P(Fe)]. Complex **3a** was precipitated as a yellowish powder by rapid addition of pentane to its solution. IR ν ($CH_2Cl_2$)/$cm^{-1}$: 2084m (PtCO); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.2 [d, P(Pt), $^{2+3}J(PP)$ 81, $^1J(PtP)$ 3319], 62.8 [d, P(Fe), $^2J(PtP)$ 34]. Complex **4a**, IR ν ($CH_2Cl_2$)/$cm^{-1}$: 1634m (acyl); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 3.2 [d, P(Pt), $^{2+3}J(PP)$ 44, $^1J(PtP)$ 5564], 63.3 [d, P(Fe), $^2J(PtP)$ 84]. Complex **5a**, IR ν ($CH_2Cl_2$)/$cm^{-1}$: 2086m (PtCO), 1676w (acyl); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.8 [d, P(Pt), $^{2+3}J(PP)$ 81, $^1J(PtP)$ 3687], 62.3 [d, P(Fe), $^{2+3}J(PtP)$ 32]. Complex **6**, $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.7 [d, P(Pd), $^{2+3}J(PP)$ 56], 65.2 [d, P(Fe)]. Complex **7**: $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ 28.9 [d, P(Pd), $^{2+3}J(PP)$ 53], 62.7 [d, P(Fe)]. Complex **8**, IR ν ($CH_2Cl_2$)/$cm^{-1}$: 2200m (PdCNR), 1648m (iminoacyl); $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ 17.2 [d, P(Pd), $^{2+3}J(PP)$ 83], 63.4 [d, P(Fe)]. Complex **9**, IR ν ($CH_2Cl_2$)/$cm^{-1}$: 1644m, 1610m (iminoacyl); $^1H$ NMR ($C_6D_6$): δ 1.71 (s, 3H, $CH_3C$), 2.13 (s, 6H, xylyl-Me), 2.18 (s, 6H, xylyl-Me), 3.44 [t, 2H, $PCH_2P$, $^2J(PH)$ 10.1], 3.86 [s, 9H, $(MeO)_3Si$]. Complex **11**, $^1H$ NMR ($C_6D_6$, 308 K): δ 1.74 (s, 3H, MeC), 4.00 [s, 9H, $(MeO)_3Si$]. Complex **12**, $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ 20.9 [d, P(Pd), $^{2+3}J(PP)$ 87], 63.1 [d, P(Fe)]. Complex **13**, IR ν ($CH_2Cl_2$)/$cm^{-1}$: 1645m (C=O → Pd); $^1H$ NMR ($CDCl_3$): δ 2.36 [s, 3H, C(O)Me], 3.64 [s, 9H, $(MeO)_3Si$]. Complex **14**, *n* = 2: IR ν (KBr)/$cm^{-1}$: 1708m (ketonic CO), 1635m (C=O → Pd); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.0 [d, P(Pd), $^{2+3}J(PP)$ 63], 63.9 [d, P(Fe)]; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.3 [s, C(O)Me], 44.1 [t, $CH_2P$, $^1J(PC)$ 18 Hz], 231.5 (s, C=O → Pd).

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