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Intermolecular alkynyl-ligand migration from aryl-palladium(II) to -platinum(II) complexes with and without a CuI catalyst. Reversible transfer of the alkynyl group between copper(I) and palladium(II) complexes

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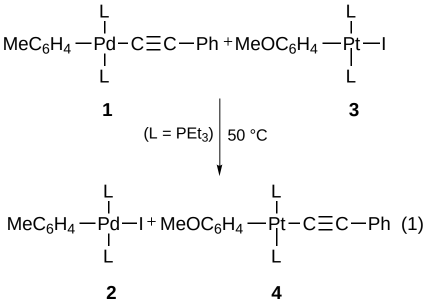
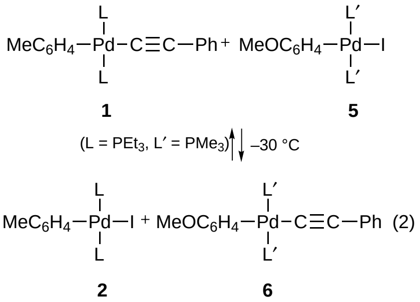
Alkynyl-ligand transfer from [PdR(C≡CPh)L$_2$] (R = C$_6$H$_4$Me-*p*, L = PEt$_3$) to [PtR′(I)L$_2$] (R′ = C$_6$H$_4$OMe-*p*), to give [PdR(I)L$_2$] and [PtR′(C≡CPh)L$_2$], has been enhanced to a large extent by addition of CuI, indicating reversible ligand transfer between Pd^{II} and Cu^{I} complexes.

Many dinuclear transition-metal complexes with bridging alkynyl ligands in a μ-η^1:η^2 fashion undergo rapid switching of the co-ordination mode as shown in Scheme 1(*i*).[1] The reaction with facile cleavage of the thermodynamically stable metal–alkynyl σ bond[2] is probably involved as a crucial step in the intermolecular transfer of an alkynyl group between one transition-metal complex and another [Scheme 1(*ii*)]. However, the latter type of alkynyl-ligand-transfer reactions have mainly been reported for transfers between alkynylcopper(I) compounds and Group 8–10 transition-metal complexes in a seemingly irreversible fashion.[3] There have been only a few reports on the intermolecular alkynyl transfer reaction among Group 8–10 metal centres.[4] In this paper we report migration of the alkynyl group from aryl(alkynyl)palladium(II) to aryl(iodo)-platinum(II) complexes in the absence and presence of a CuI catalyst and describe the role of CuI in the reaction.

An aryl(alkynyl)palladium(II) complex, *trans*-[Pd(C$_6$H$_4$-Me-*p*)(C≡CPh)(PEt$_3$)$_2$] **1**, prepared from the reaction of *trans*-[Pd(C$_6$H$_4$Me-*p*)(I)(PEt$_3$)$_2$] **2** and [{Cu(C≡CPh)(PPh$_3$)}$_4$][3h,5] at −30 °C, reacts smoothly at 50 °C with equimolar amounts of *trans*-[Pt(C$_6$H$_4$OMe-*p*)(I)(PEt$_3$)$_2$] **3** to give a mixture of **2** and *trans*-[Pt(C$_6$H$_4$OMe-*p*)(C≡CPh)(PEt$_3$)$_2$] **4** quantitatively [equation (1)].† The NMR (^{1}H and ^{31}P-{^{1}H}) spectra of the reaction mixture show only the peaks due to complexes **1**–**4** throughout the reaction, indicating that the aryl groups behave as spectator ligands and do not undergo migration between the metal centres in contrast to the aryl ligands bonded to several Ni^{II} and Pd^{II} complexes.[6] The reaction (1) obeys the kinetics that is first-order both in [**1**] and [**3**] with a rate constant 1.13 × 10^{-2} dm^3 mol^{-1} s^{-1} at 50 °C. Similar reaction between palladium complexes **1** and *trans*-[Pd(C$_6$H$_4$OMe-*p*)(I)(PMe$_3$)$_2$] **5** at −30 °C initially gives **2** and *trans*-[Pd(C$_6$H$_4$OMe-*p*)(C≡CPh)-(PMe$_3$)$_2$] **6** as shown in equation (2).‡ The alkynyl-ligand transfer occurs prior to intermolecular aryl ligand migration both in reactions (1) and (2).



(1)



(2)

Reaction (1) is significantly enhanced by addition of CuI (2.09 μmol dm^{-3}, [Cu]/[Pd] = 0.10) and is completed within 5 min at 50 °C. The results indicate that the reaction proceeds through two independent pathways as shown in Scheme 2. Pathway (*i*) involves direct ligand exchange, possibly having a bimetallic transition state, while (*ii*) has the alkynylcopper(I) intermediate that promotes the indirect ligand transfer from Pd to Pt. The latter pathway requires alkynyl-ligand transfer from the Pd^{II} to one Cu^{I} centre, but this reaction is unprecedented. Addition of

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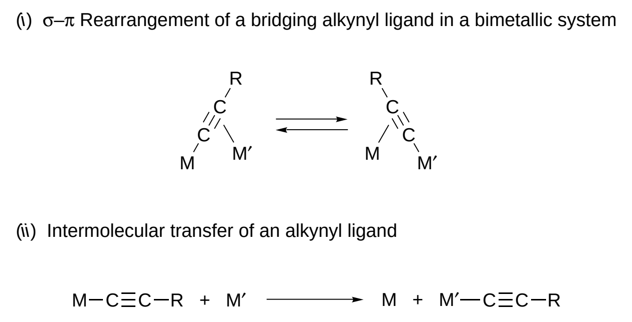
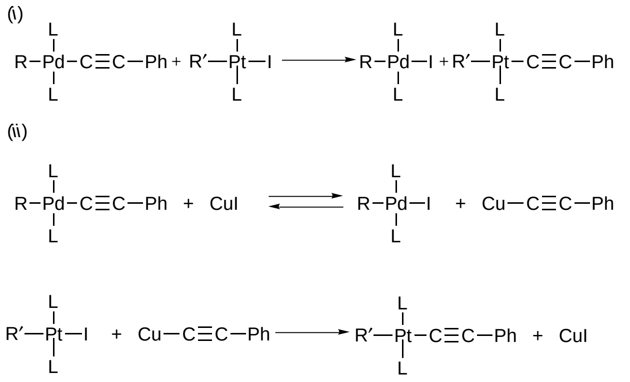
† Spectroscopic data for **1**. IR (KBr): ν(C≡C) 2092 cm^{-1}. ^{1}H NMR (400 MHz in C$_6$D$_6$): δ 0.98 (m, 18 H, CH$_3$), 1.57 (m, 12 H, PCH$_2$), 2.29 (s, 3 H, CH$_3$), 7.00 (t, 1 H, C$_6$H$_4$*H*, *J* = 7), 7.08 (d, 2 H, C$_6$H$_3$*H*$_2$, *J* = 7), 7.16 (t, 2 H, C$_6$H$_3$*H*$_2$, *J* = 7 Hz), 7.46 and 7.62 (d, 4 H, C$_6$H$_4$, *J* = 7 Hz). ^{13}C-{^{1}H} NMR (100 MHz in C$_6$D$_6$): δ 119.0 (t, PdC≡, *J* = 20 Hz), 111.6 (s, ≡*C*−C). ^{31}P-{^{1}H} NMR (160 MHz in C$_6$D$_6$): δ 14.5 (s). **2**. ^{1}H NMR (400 MHz in C$_6$D$_6$): δ 0.89 (m, 18 H, CH$_3$), 1.56 (m, 12 H, PCH$_2$), 2.18 (s, 3 H, CH$_3$), 6.90 and 7.21 (d, 4 H, C$_6$H$_4$, *J* = 7 Hz). ^{31}P-{^{1}H} NMR (160 MHz in C$_6$D$_6$): δ 10.3 (s). **3**. ^{1}H NMR (400 MHz in C$_6$D$_6$): δ 0.87 (m, 18 H, CH$_3$), 1.71 (m, 12 H, PCH$_2$), 3.43 (s, 3 H, OCH$_3$), 6.77 and 7.32 (d, 4 H, C$_6$H$_4$, *J* = 8 Hz). ^{31}P-{^{1}H} NMR (160 MHz in C$_6$D$_6$): δ 8.9 [s, *J*(PtP) = 1364 Hz]. **4**. IR (KBr): ν(C≡C) 2098 cm^{-1}. ^{1}H NMR (400 MHz in C$_6$D$_6$): δ 0.96 (m, 18 H, CH$_3$), 1.66 (m, 12 H, PCH$_2$), 3.50 (s, 3 H, OCH$_3$), 6.96 (d, 2 H, C$_6$H$_4$, *J* = 7), 7.02 (t, 1 H, C$_6$H$_4$*H*, *J* = 7), 7.17 (t, 2 H, C$_6$H$_3$*H*$_2$, *J* = 7), 7.48 (d, 2 H, C$_6$H$_2$*H*$_2$, *J* = 7), 7.61 (d, 2 H, C$_6$H$_2$*H*$_2$, *J* = 7 Hz). ^{31}P-{^{1}H} NMR (160 MHz in C$_6$D$_6$): δ 10.2 [s, *J*(PtP) = 1320 Hz]. ^{13}C-{^{1}H} NMR (100 MHz in CD$_2$Cl$_2$): δ 55.1 (OCH$_3$), 109.9 [≡*C*−C, *J*(PtC) = 22], 113.7 [*C*H−C−Pt, *J*(PtC) = 50], 114.3 [Pt−C≡, t, *J*(PC) = 15, *J*(PtC) = 890], 124.8 (*para* carbon of C≡CC$_6$H$_5$), 128.2, 130.0 [≡C−*C*, *J*(PtC) = 22], 131.0, 139.1, 145.0 [Pt−C, t, *J*(PC) = 10, *J*(PtC) = 673 Hz], 155.5 (OC). **5**. ^{1}H NMR (400 MHz at −30 °C in CD$_2$Cl$_2$): δ 1.19 (apparent triplet due to virtual coupling, 18 H, CH$_3$), 3.683 (s, 3 H, OCH$_3$), 6.67 and 7.05 (d, 4 H, C$_6$H$_4$, *J* = 8 Hz). ^{31}P-{^{1}H} NMR (160 MHz at 25 °C in C$_6$D$_6$): δ −21.0 (s). **6**. ^{1}H NMR (400 MHz at −30 °C in CD$_2$Cl$_2$): δ 1.19 (apparent triplet due to virtual coupling, 18 H, CH$_3$), 3.676 (s, 3 H, OCH$_3$), 6.63 and 7.13 (d, 4 H, C$_6$H$_4$, *J* = 8), 7.18 (t, 1 H, C$_6$H$_4$*H*, *J* = 7), 7.34 (d, 2 H, C$_6$H$_3$*H*$_2$, *J* = 7), 7.54 (t, 2 H, C$_6$H$_3$*H*$_2$, *J* = 7 Hz). ^{31}P-{^{1}H} NMR (160 MHz at −30 °C in CD$_2$Cl$_2$): δ −17.3 (s).

‡ The NMR spectra of the reaction mixture after 1 h at −30 °C showed conversion of *ca.* 10% of **1** and **5** into **2** and **6**, while raising the temperature caused formation of many Pd complexes probably due to accompanying exchange of the phosphine ligands among the complexes.

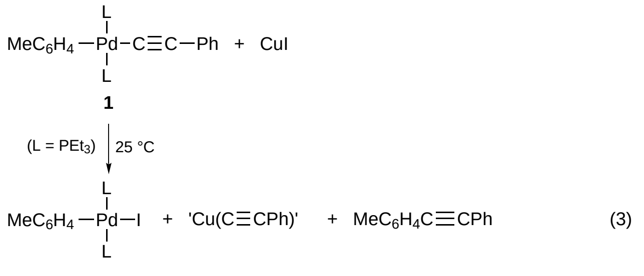


Scheme 1



Scheme 2

CuI to a benzene solution of an equimolar amount of compound **1** at 25 °C results in the formation of **2** and $MeC_6H_4C{\equiv}CPh$ as shown in Fig. 1. Although the NMR spectra of the reaction mixture do not give clear evidence for the formation of $[\{Cu(C{\equiv}CPh)\}_n]$, which should be generated by the alkynyl-ligand transfer, similar reaction in the presence of PPh_3 (3 equivalents of PPh_3 per 1 equivalent of **1**) gives $[Cu(C{\equiv}CPh)(PPh_3)_3]$ as the isolable product. The results indicate clearly that the alkynyl ligand in the aryl(alkynyl)palladium(II) complex easily migrates to the Cu^I centre under the conditions shown in equation (3). Formation of $MeC_6H_4C{\equiv}CPh$ in this reaction may



1

2

be ascribed to reductive elimination from *cis*-$[Pd(C_6H_4Me\text{-}p)(C{\equiv}CPh)(PEt_3)_2]$ which is partly formed by the *cis–trans* isomerization of **1** under these conditions.§

The present study has disclosed alkynyl-ligand transfer from Pd^{II} to Pt^{II} centres in a direct fashion as well as through an intermediate alkynylcopper(I) complex. Reversible transfer of the ligand between Cu^I and Pd^{II} metal centres has been observed directly. Aryl(alkynyl)palladium(II) complexes in this study have been postulated as the possible intermediates in the cross-coupling reaction of aryl halides with terminal alkynes catalysed by Pd complexes in the presence of CuI[8] but their chemical properties have not been reported so far.[9]

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research of Ministry of Education, Science, Culture and Sports, Japan.

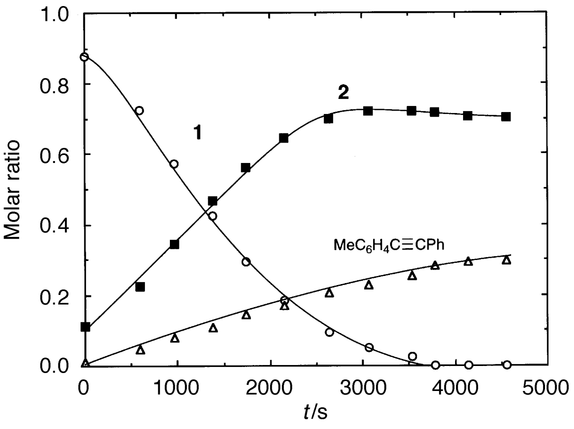


Fig. 1 Profile of the reaction of compound **1** (27.4 mmol dm^{-3}) with CuI (26.3 mmol dm^{-3}) at 25 °C in C_6D_6. Amounts of **1** and the resulting **2** and $MeC_6H_4C{\equiv}CPh$, shown by the molar ratios based on the initial molarity of **1**, were obtained by relative peak area ratio in the ^1H NMR spectra

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Received 2nd *January* 1997; *Communication* 7/00021I

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§ *cis–trans* Isomerisation of Pd^{II} complexes induced by intermolecular ligand exchange has been reported.[7]