

$[cis-Pt(C_6F_5)_2(C\equiv CPh)_2]^{2-}$ as a Double Alkynyl Transfer Reagent. Synthesis and Characterization of the Ir(III)–Pt(II) Tweezer Complex $\{[(\eta^5-C_5Me_5)(PEt_3)Ir(C\equiv CPh)_2]Pt(C_6F_5)_2\}$

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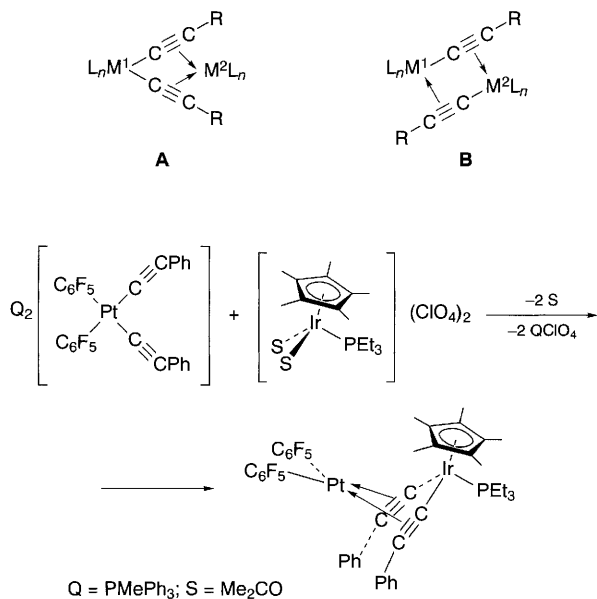
$[cis-Pt(C_6F_5)_2(C\equiv CPh)_2]^{2-}$ reacts with $[Ir(C_5Me_5)(PEt_3)(Me_2CO)_2](ClO_4)_2$, via a double alkylation process, yielding $\{[(\eta^5-C_5Me_5)(PEt_3)Ir(C\equiv CPh)_2]Pt(C_6F_5)_2\}$ in which the alkynyl groups are σ bonded to the iridium centre and π bonded to the platinum one.

A number of recent studies have revealed the ability of σ -bis(alkynyl)complexes to form homo- and hetero-dinuclear doubly alkynyl bridging compounds¹ which have been widely studied, both experimentally and theoretically in the last few years.² Usually, in the resulting complexes the $L_nM(C\equiv CR)_2$ used as starting material is acting as a chelating ligand to the second metal centre (A) and only in a few cases, transfer of one of the acetylide ligands to the second metal atom takes place, thus resulting in the formation of a symmetrical^{1e,f} (B) or unsymmetrical^{1g} double bridging μ - $\eta^{1:2}$ alkynyl system. The driving force for this alkynyl transfer process, is not clear. Thus, we have recently reported that $[(C_5H_5)_2Ti(C\equiv CBu^t)_2]^{1g}$ acts as a mono alkynyl transfer reagent towards $[Pt(C_2H_4)(PPh_3)_2]$, but the analogous $[(C_5H_5)_2Ti(C\equiv CPh)_2]$ acts only as a chelating ligand in the reaction with $[Pt(C_2H_4)(PPh_3)_2]^{1g}$ or $[Pt(C_2H_4)_2(PPh_3)]^{1h}$. On the other hand, it also seems rather surprising that the anion $[cis-Pt(C_6F_5)_2(C\equiv CR)_2]^{2-}$ acts as an alkynylating agent in the reaction with the neutral $[cis-M(C_6F_5)_2(thf)_2]$ ($M = Pd, Pt$) complexes^{1j} (type B) while acts as a chelating ligand (type A) when it reacts with the very electrophilic species HgX_2 ($X = Cl, Br, I$)¹ⁱ or $[M(\eta^3-allyl)]^+$ ($M = Pd, Pt$).^{1c}

In this communication we report the reaction (1:1 molar ratio) between $(PMePh_3)_2[cis-Pt(C_6F_5)_2(C\equiv CPh)_2]$ and the solvento complex $[Ir(C_5Me_5)(PEt_3)(Me_2CO)_2](ClO_4)_2$ (prepared *in situ*), which results in an unexpected double alkylation process, yielding the novel neutral derivative $\{[(\eta^5-C_5Me_5)(PEt_3)Ir(C\equiv CPh)_2]Pt(C_6F_5)_2\}$ **1**† (yellow, air stable, 60% yield) in which the resulting neutral unit $Ir(C_5Me_5)(PEt_3)(C\equiv CPh)_2$ is acting as a chelating metalloligand towards the fragment $Pt(C_6F_5)_2$ (Scheme 1). Analytical, mass

spectral and ¹H, ¹³C, ¹⁹F and ³¹P NMR data† are in accord with this formulation.

The presence of bridging alkynyl ligands can be easily inferred from the observation in its IR spectrum of two medium $\nu(C\equiv C)$ absorptions (2030 and 1971 cm^{-1}) at lower frequencies than those observed for the mononuclear $[cis-Pt(C_6F_5)_2(C\equiv CPh)_2]^{2-}$ precursor and in the range expected for carbon–carbon triple bond side-on coordinated to a transition metal.¹ In order to obtain further structural information about the bonding features of the alkynyl ligands in this compound, a single-crystal X-ray study‡ was carried out. The molecular structure (Fig. 1) shows that both alkynyl ligands are σ -bonded to the Ir centre, the Ir–C(13) [1.97(2) Å] and the Ir–C(21) [1.99(2) Å] distances being similar to the reported values in $[Ir_2Cu_4(C\equiv CPh)_8(PPh_3)_2]^{4b}$ (average 2.044 Å), $[Fe_2Ir(\mu^3-\eta^2-C\equiv CPh)(CO)_8(PPh_3)]$ [1.93(1) Å]^{4a} and $[(COD)Ir(\mu-\eta^{1:2}-C\equiv CSiMe_3)]_2$ [1.98(2), 2.01(1) Å].^{2g} The alkynyl groups are also attached by η^2 -bridging to the Pt atom. The Pt–C distances to the inner C(13), C(21) and outer C(14), C(22) acetylenic carbon atoms are quite similar to those found in $\{Pt(dppe)(C\equiv CPh)_2\}Pt(C_6F_5)_2$.^{1f} The C≡C bond lengths [1.21(3) and 1.21(3) Å] and angles of the acetylenic skeletons



Scheme 1

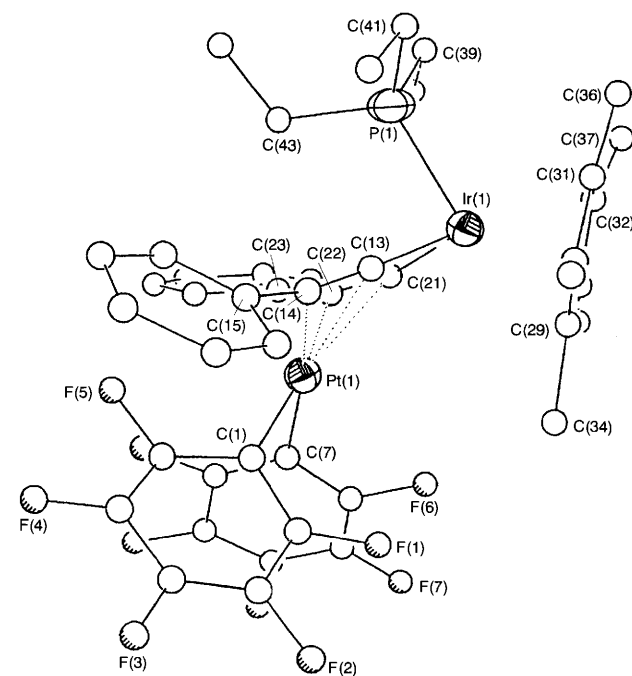


Fig. 1 Molecular structure of $\{[(\eta^5-C_5Me_5)(PEt_3)Ir(C\equiv CPh)_2]Pt(C_6F_5)_2\}$ with the atomic numbering scheme. Selected bond lengths (Å) and angles ($^\circ$): Ir–P(1) 2.29(1), Ir–C(13) 1.97(2), Ir–C(21) 1.99(2), C(13)–C(14) 1.21(3), C(21)–C(22) 1.21(3), Pt–C(13) 2.41(2), Pt–C(14) 2.38(2), Pt–C(21) 2.46(2), Pt–C(22) 2.30(2), Pt–C(1) 1.97(2), Pt–C(7) 2.00(2), Ir–C(13)–C(14) 176.9(2), Ir–C(21)–C(22) 160.9(2), C(13)–C(14)–C(15) 156.8(2), C(21)–C(22)–C(23) 154.2(2).

[Ir-C_α-C_β 176.9(2) and 160.9(2)°, C_α-C_β-Ph 156.8(2)° and 154.2(2)°] are similar to those found in related systems.^{1f}

The Pt atom is located in a distorted square planar environment [formed by the C_{ipso} atoms of the C₆F₅ groups and the midpoints of the C≡C triple bonds] and the Ir centre is in a pseudooctahedral environment formed by C(13), C(21) and P(1) atoms and the η⁵-coordinated pentamethylcyclopentadienyl ligand. The Pt-Ir distance, 3.51(1) Å, excludes any significant intermetallic interaction.

Further investigations of the reactivity of σ-bis(alkynyl)platinum complexes towards cationic Rh and Ir^{I,III} solvent species are now in progress.

We thank the Dirección General de Investigación Científica Técnica (Spain) [Project PB92-0364 and a grant to J. R. B.] for financial support.

Received, 16th March 1995; Com. 5/01686J

Footnotes

† *Experimental details for 1.* All manipulations were carried out under a nitrogen atmosphere. Solvents were dried by standard procedures and distilled under dry N₂ before use. A red solution of [Ir(C₅Me₅)Cl₂(PEt₃)] (0.088 g, 0.17 mmol) in acetone (20 cm³) was treated with (0.071 g, 0.34 mmol) of AgClO₄ and the mixture was stirred at room temp. for 1 h filtered through Kieselgurh. The resulting pale-orange solution, which contains [Ir(C₅Me₅)(PEt₃)(Me₂CO)₂][ClO₄]₂, was concentrated to ca. 10 cm³ and [PMePh₃]₂[cis-Pt(C₆F₅)₂(C≡CPh)₂]³ (0.2 g, 0.16 mmol) was added to give immediately a deep orange solution which was stirred for 15 min. Evaporation of the solution to dryness and treatment with EtOH (ca. 5 cm³) affords complex **1** as a yellow microcrystalline solid (0.12 g, 62% yield); Ir: ν(C≡C/cm⁻¹ 2031(s), 1971(s), ν(C₆F₅)x-sens/cm⁻¹ 802(vs), 792(vs); ¹H NMR (300 MHz, CDCl₃, SiMe₄, 293 K): δ 7.06 (m, 10 H, C≡CPh), 2.16 (d, 15 H, C₅Me₅, ⁴J_{P-H} 1.9 Hz), 1.95 (m, 6H, CH₂, PEt₃), 0.96 (m, 9 H, Me, PEt₃); ¹³C NMR: δ 147.8, 144.75, 137.4, 134.2 (m, br, C₆F₅), 130.9, 126.9 (both s, Ph), 126.5 (s, C_{para}, Ph), 125.5 (s, C_{ipso}, Ph), 98 (s, C_β), 97.8 (d, C₅Me₅, ²J_{C-P} 2.6 Hz), 55.3 (d, C_α, ²J_{C-P} 17 Hz), 14.7 (d, PCH₂Me, ¹J_{C-P} 36 Hz), 9.26 (s, C₅Me₅), 6.76 (d, PCH₂Me, ²J_{C-P} 2.8 Hz); ¹⁹F NMR (CFCl₃): δ -114.9 (s br, 2 F_{ortho}), -119.3 (s br, 21 F_{ortho}) (Pt satellites due to ³J_{Pt-F_{ortho}} are observed but are not well resolved), -164.9 (t, 2 F_{para}), -165.9, -166.5 (s br, overlapping, 4 F_{meta}); ³¹P NMR (HDA, 85% H₃PO₄): δ 5.83; EI-MS: m/z = 1176 [M⁺] (10%).

‡ *Crystal data for 1.* Suitable crystals of **1** were obtained by cooling a concentrated solution of **1** in acetone at -30 °C. C₄₄H₄₀F₁₀P Ir Pt, M_r = 1177.05, orthorhombic, space group Pna2₁, a = 19.649(1), b = 10.482(1), c = 20.102(2) Å, U = 4140.1 Å³, Z = 4, D_c = 1.88 g cm⁻³, λ(Mo-Kα) = 0.71073 Å, μ = 6.75 mm⁻¹, F(000) = 2256, T = 298 K, crystal dimensions

= 0.2 × 0.5 × 0.5 mm, Stoe AED2 Siemens diffractometer, ω-θ scan technique. Standard Patterson method. Full-matrix least-squares refinement (SHELXTL-PLUS⁵). Anisotropic thermal parameters for all non-hydrogen atoms, except for (C₅Me₅). Absorption correction was based on psi-scan measurements. The enantiomorph was chosen on the basis of a lower wR factor. The final wR = 0.0633, conventional R = 0.0473 for 3173 data with F ≥ 4 σ F₀ and 463 parameters. Weighting scheme, w = 1/σ²F = 0.001783F². The largest difference peak and trough had densities of +1.35, -1.71 e Å⁻³, we attribute the size of these values to series termination and perhaps residual absorption effects. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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