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Formation of an Unsymmetrical Pt−Ir Tetraalkynyl Complex and Investigation into Subsequent Construction of Multimetallic Systems[†]

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The reactions between $[Pt(C{\equiv}CR)_4]^{2-}$ (R = Ph, *t*-Bu, $SiMe_3$) and $[Ir(\mu\text{-}Cl)(COD)]_2$ have been studied, but the formation of an unsymmetrical heterobinuclear complex $(NBu_4)[(COD)Ir(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)Pt(C{\equiv}CSiMe_3)_2]$, $(NBu_4)[\{Ir{-}Pt\}(C{\equiv}CSiMe_3)_2]$, **1** was only observed with the homoleptic species $[Pt(C{\equiv}CSiMe_3)_4]^{2-}$. Complex **1** exhibits in the solid state a bent σ,π double-alkynyl bridging system, which is formed through a migration of one σ-alkynyl group from platinum to iridium. The stability of the remaining Pt-acetylide σ-bonds in **1** and its possible application in the assembly of multimetallic compounds containing the {Ir−Pt} "pincer" unit has been investigated. Treatment of $(NBu_4)[\{Ir{-}Pt\}(C{\equiv}CSiMe_3)_2]$ (**1**) with neutral $[cis\text{-}M(C_6F_5)_2(THF)_2]$ (THF = tetrahydrofuran, M = Pt, Pd) or cationic $[Rh(COD)(acetone)_x]^+$ or $[Pd(\eta^3\text{-}C_3H_5)S_x]^+$ solvento species (the latter generated "in situ") leads to very unusual anionic $(NBu_4)[\{Ir{-}Pt\}(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2M(C_6F_5)_2]$ (M = Pt, **2**; Pd, **3**) or neutral heterotrimetallic complexes $[\{Ir{-}Pt^-\}(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Rh^+(COD)]$ (**4**) and $[\{Ir{-}Pt^-\}(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Pd^+(\eta^3\text{-}C_3H_5)]$ (**5**), respectively. The molecular structure of **4** confirms the presence of a formally heterotrimetallic zwitterion $[(COD)Ir(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)Pt^-(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Rh^+(COD)]$, formed by the binuclear anionic fragment $[(COD)Ir(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)Pt(C{\equiv}CSiMe_3)_2]^-$, which in its turn acts as a chelating dimetallo bidentate ligand toward the cationic $[Rh(COD)]^+$ unit. However, a similar neutralization reaction of **1** with 1 equiv of $AgClO_4$ produces an unusual hexanuclear trimetallic complex $[(\eta^2\text{-}\{Ir{-}Pt\}(C{\equiv}CSiMe_3)_2)_2Ag_2]$ (**6**), in which the heterobimetallic diyne anionic substrate $[\{Ir{-}Pt\}(C{\equiv}CSiMe_3)_2]^-$ acts as a $\mu\text{-}\eta^2{:}\eta^2$ bridging ligand of two different silver(I) centers.

Introduction

Compounds containing metal centers bridged by carbon rich ligands are currently attracting much interest because of their potential novel material properties, as well as their inherent theoretical interest.[1] Within this field, transition metal σ-alkynyl complexes have proved to be particularly fruitful as building blocks for molecular materials because of the interesting electronic communication between metal centers in bi-, oligo-, or polymetallic compounds.[2]

The chemistry of organometallic substituted alkynes or metalloalkynes $[M](C{\equiv}CR)_n$ (n = 1, 2) has also drawn considerable attention with regard to their structural aspects and reactivity.[3] Quite often, a metal−σ-bis(alkynyl) compound is associated with a second metal fragment "L_nM" through η^2-alkyne interactions,[3c,d,4] and, as it has been pointed out, this approach is a powerful method for stabilizing unusual organometallic entities.[4a−c] The resulting double-alkynyl bridged complexes, also generated through the activation of 1,3-butadiynes with metallocene sources,[5] have been extensively examined with the aim of understanding not only metal−ligand interactions but also metal−metal interactions and metal−metal cooperation in C−C coupling or cleavage bond reactions.[5,6] In contrast to this, the chemistry of metal polyacetylides $[M](C{\equiv}CR)_n$ (n = 3−6) has been explored to a much lesser extent, and the association, in a single molecule, of three or more metals connected by double-alkynyl bridging systems is more unusual.[4a,i,6c,7,8]

We have been interested for several years in systematic studies of the interaction of σ-alkynyl platinum complexes with metal substrates containing labile ligands

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[†] Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.

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in order to gain a better understanding of the factors that determine the final σ,π disposition of the alkynyl bridging groups. These studies have not been limited to neutral or anionic bis(alkynyl) platinum compounds, which usually lead to heterobinuclear double-alkynyl bridged compounds,[3d,4d,g,10] but have also covered the homoleptic tetra(alkynyl)platinate(II) species $[Pt(C\equiv CR)_4]^{2-}$, allowing us to isolate a variety of di- and trinuclear compounds.[8] Previous works had shown that these anions form simple 1:2 adducts $[\{Pt(C\equiv CR)_4\}\{ML_n\}_2]$ with d^{10} [$CdCl_2$,[8g] HgX_2,[8a] MX (M = Cu, Ag; X = Cl, Br)[8c]] or d^7 ($CoCl_2$)[8b] metal salts, but act as monoalkynylating agents toward only one of the two neutral d^8 “*cis*-$Pt(C_6F_5)_2$” associated units in the final trinuclear anionic derivatives $[(C_6F_5)_2Pt(\mu\text{-}C\equiv CR)_2Pt(\mu\text{-}C\equiv CR)_2Pt(C_6F_5)_2]^{2-}$.[11] The only documented examples of double-alkynyl migration processes were recently observed by us[4a,9d] with the solvento dicationic d^6 metal fragments $[MCp^*(PEt_3)S_2]^{2+}$ (M = Rh, Ir), yielding binuclear compounds in which the resulting neutral fragments “$MCp^*(C\equiv CR)_2(PEt_3)$” and “*cis*-$Pt(C\equiv CR)_2$”, respectively, are held together by η^2-Pt–bis(alkyne) interactions.[4a] Surprisingly, in similar reactions with two cationic units “$Pd(\eta^3\text{-}C_3H_5)^+$” or “$Rh(COD)^+$” we have also found that the platinum center retains the σ-coordination to the alkynyl groups, while the second raw d^8 metals are stabilized by η^2-alkyne interactions.[8d,e]

Continuing with our research in this direction, we studied the interaction of these anions $[Pt(C\equiv CR)_4]^{2-}$ (R = Ph, *t*-Bu, $SiMe_3$) with the related iridium d^8 metal fragment “$Ir(COD)^+$”, and in this paper we discuss the synthesis of an unsymmetrical σ,π double-alkynyl bridged iridium–platinum complex, $(NBu_4)[(COD)Ir(\mu\text{-}1\kappa C^\alpha{:}\eta^2\text{-}C\equiv CSiMe_3)(\mu\text{-}2\kappa C^\alpha{:}\eta^2\text{-}C\equiv CSiMe_3)Pt(C\equiv CSiMe_3)_2]$ (**1**), formed via migration of one alkynyl group from Pt to Ir. This complex still contains two terminal alkynyl ligands bonded to Pt, and, therefore, the possibility of forming higher multimetallic assemblies has been in-

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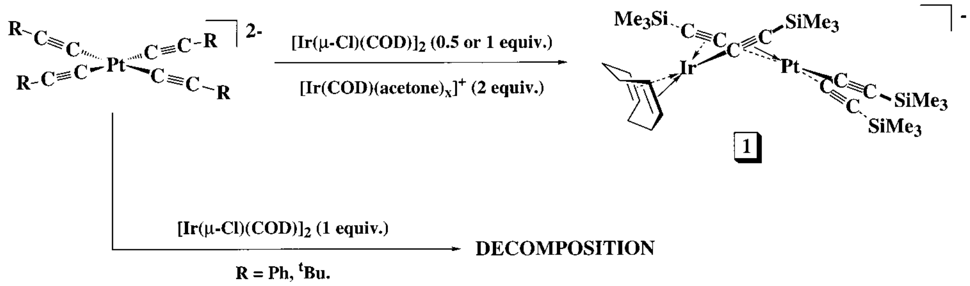
Scheme 1



vestigated. Metallic fragments "$M(C_6F_5)_2$" (M = Pt, Pd), $Pd(\eta^3\text{-}C_3H_5)$ and Rh(COD) and Ag^+ cations can be easily attached via η^2-coordination, yielding unusual heterotrimetallic (**2**−**5**) or hexametallic **6** compounds.

Results and Discussion

(i) Synthesis. All efforts to prepare a defined product by reacting $(NBu_4)_2[Pt(C{\equiv}CR)_4]$ (R = Ph, *t*-Bu) with $[Ir(\mu\text{-}Cl)(COD)]_2$ in acetone were fruitless. The reactions evolve yielding very dark solutions from which only mixtures of undefined products were isolated. In contrast, as shown in Scheme 1, the anionic Ir−Pt complex $(NBu_4)[\{Ir{-}Pt\}(C{\equiv}CSiMe_3)_2]$ (**1**) is readily obtained as an air-stable yellow microcrystalline solid by treatment of $(NBu_4)_2[Pt(C{\equiv}CSiMe_3)_4]{\cdot}2H_2O$ with 0.5 equiv of $[Ir(\mu\text{-}Cl)(COD)]_2$ in acetone. However, despite the presence of extra alkynyl ligands, we have not succeeded in obtaining the desired trinuclear neutral complex $[(COD)Ir(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Ir(COD)]$, despite our many attempts. Treatment of $(NBu_4)_2[Pt(C{\equiv}CSiMe_3)_4]{\cdot}2H_2O$ with 1 equiv of $[Ir(\mu\text{-}Cl)(COD)]_2$ under the same conditions afforded the binuclear complex **1** (51% yield), and complex **1** is also the only species isolated as a pure compound by mixing an acetone solution of $[Pt(C{\equiv}CSiMe_3)_4]^{2-}$ with 2 equiv of the solvento $[Ir(COD)S_2](ClO_4)$ species in acetone, although in rather low yield (19%). The results summarized in Scheme 1 confirm the considerable inertness of anion **1**, preventing it from acting again as an alkynylating agent or coordinating a second cationinc "$Ir(COD)^+$" unit. These results contrast with previous studies that have shown that $[Pt(C{\equiv}CR)_4]^{2-}$ (R = $SiMe_3$, *t*-Bu) are good precursors for the synthesis of neutral trinuclear adducts of the $[\{Pt(C{\equiv}CR)_4\}\{Rh(COD)\}_2]$[8e] type and indicate the stronger tendency of Ir to form $\sigma\text{-}Ir{-}C{\equiv}CR$ bonds compared to Rh and that it is easier to attach a Rh(I) center via η^2-alkyne coordination than an Ir(I) one.

The formulation given in Scheme 1 for complex **1**, which implies the migration of a $\sigma\text{-}C{\equiv}CSiMe_3$ group from Pt to Ir forming a σ/π double-alkynyl bridging system, agrees with its spectroscopic data (IR, NMR) and has been confirmed by a single-crystal X-ray diffraction study. Bi- or polynuclear species containing terminal alkynyl ligands are rather rare.[4h,7f,11,12] We have recently reported related Rh/Ir−Pt ($d^6{-}d^8$) neutral compounds[4a] $[(PEt_3)Cp^*M(\mu\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2]$, but in this case the "$Pt(C{\equiv}CR)_2$" unit is η^2-attached to both alkynyl bridging ligands, which are σ-bonded to the electrophilic d^6 metal center. In contrast to these $d^6{-}d^8$ derivatives which exhibited a very limited stability in solution, complex **1** is remarkably stable, and this prompted us to explore the stability of the remaining Pt−acetylide σ-bonds to further migrations and its potential as precursor for higher nuclearity systems. The results of this study are presented in Scheme 2. The capability of *cis*-bis(alkynyl)mononuclear platinum species to stabilize η^2-bis(alkyne) interactions in d^8 neutral "*cis*-$M(C_6F_5)_2$" (M = Pt, Pd)[4a,d,9a] and cationic "$Rh(COD)^+$"[8e] and "$Pd(\eta^3\text{-}C_3H_5)^+$"[8d,9c] metal fragments has already been well established. The resulting double-alkynyl bridging system typically adopts a chelating-type bent (V-shape) structural disposition.

Accordingly, $(NBu_4)[\{Ir{-}Pt\}(C{\equiv}CSiMe_3)_2]$ (**1**) was reacted with equimolecular amounts of the bis(solvento) neutral complexes [*cis*-$M(C_6F_5)_2(THF)_2$] (M = Pt, Pd; THF = tetrahydrofuran), and, in another approach, **1** was also reacted with the cationic species $[Rh(COD)(acetone)_x]^+$ and $[Pd(\eta^3\text{-}C_3H_5)(acetone)_x]^+$, prepared in situ, in acetone. As expected, these reactions lead to the formation of unusual heterotrimetallic anionic $(NBu_4)[\{Ir{-}Pt\}(\mu\text{-}2\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2M(C_6F_5)_2]$ (M = Pt **2**, Pd **3**) or neutral $[\{Ir{-}Pt^-\}(\mu\text{-}2\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Rh^+(COD)]$ (**4**) and $[\{Ir{-}Pt^-\}(\mu\text{-}2\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Pd^+(\eta^3\text{-}C_3H_5)]$ (**5**) complexes, which are isolated as yellow (**2**, **3**, **5**) or orange (**4**) solids in moderate yields (41−65%). All these reactions consist of the replacement of the weakly coordinated solvent molecules by the η^2-alkyne interactions, leading to trimetallic species that contain two different types of bridging systems. Crystals of **4** were grown at low temperature from a CH_2Cl_2/hexane solution, and its crystal structure (see below) confirms the presence of a slightly bent σ/π double-alkynyl bridging system connecting the iridium and platinum atoms, and a strongly bent chelating-type (V shape) bridging system between platinum and rhodium. Within these building blocks, the binuclear anionic entity {Ir−Pt} maintains its structural disposition as is also suggested for the remaining derivatives on the basis of their spectroscopic data.

In another approach, **1** was also reacted with silver(I) (as $AgClO_4$), which has been previously used by us to sandwich square-planar alkynyl platinate entities through η^2-Ag−acetylide linkages.[13] A hexametallic neutral complex is obtained when 1 equiv of $AgClO_4$ is

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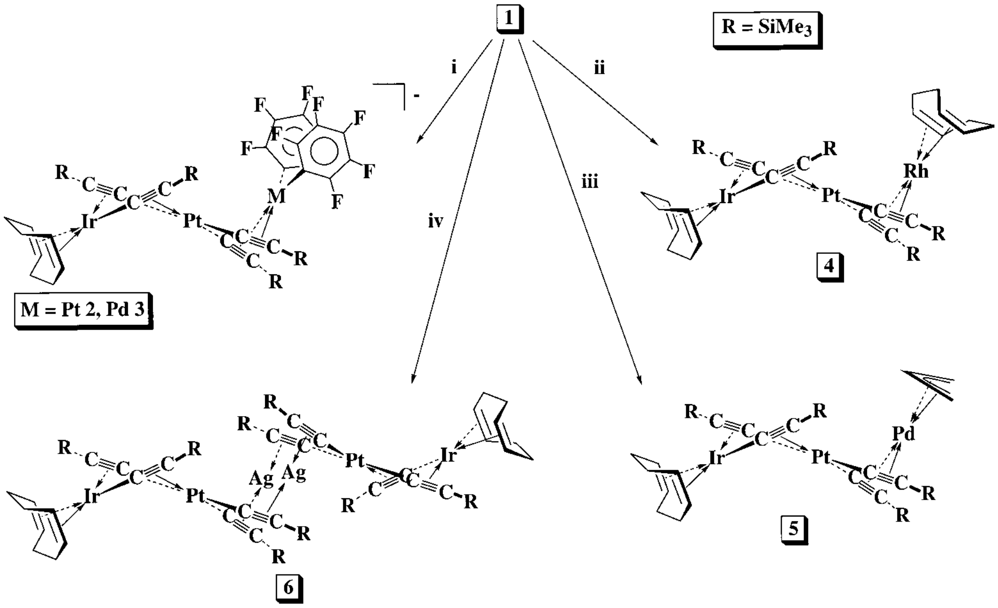
Scheme 2



i) + [*cis*-M(C_6F_5)$_2$(THF)$_2$]; ii) + [Rh(COD)(acetone)$_x$]$^+$; iii) + 1/2 [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ + $NaClO_{4(excess)}$; iv) + $AgClO_4$.

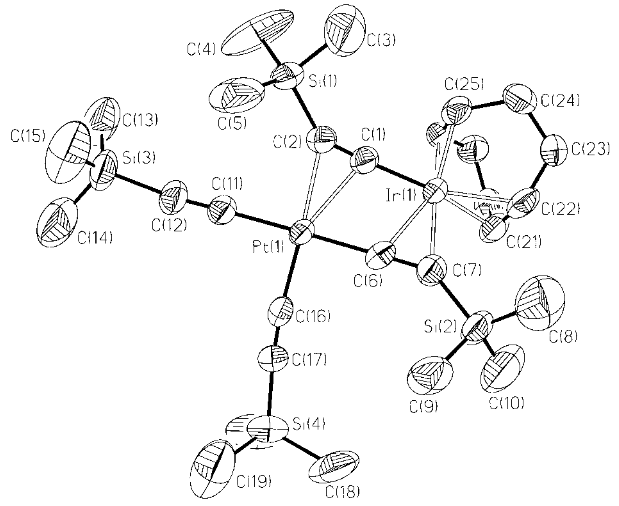


Figure 1. View of the molecular structure of the anion of complex **1**·0.25CH_2Cl_2, showing the atom-numbering scheme. Hydrogen atoms have been omitted for clarity.

treated with (NBu_4)[{Ir−Pt}(C≡$CSiM_3$)$_2$] in acetone at low temperature (253 K) (Scheme 2). Complex [(η^2-{Ir−Pt}(C≡$CSiMe_3$)$_2$)$_2$$Ag_2$] (**6**) was obtained as a deep orange microcrystalline solid in a 67% yield and characterized by usual analytic and spectroscopic methods (see below).

While, like the precursor **1**, complexes **2**−**5** are stable for extended periods in solution (low temperature) and in the solid state, the hexametallic species **6** is stable in the solid state, but decomposes readily in solution.

(ii) Structural Characterization. (a) Structural Studies. The structure of the heterobimetallic [(COD)Ir(μ-1κC^α:η^2-C≡$CSiMe_3$)(μ-2κC^α:η^2-C≡$CSiMe_3$)Pt(C≡$CSiMe_3$)$_2$]$^-$ anion of **1** is shown in Figure 1. Relevant bond distances and angles are collected in Table 1. The structure provides clear evidence for the σ-alkynyl migration from platinum to iridium. The structural details of the resulting σ(Pt,Ir)/π(Ir,Pt) double-alkynyl bridging system are very much in the expected range, as established by comparable homo-[9a,b,14] and heterobinuclear compounds.[4a,10] In particular, and in agreement with previous observations made in [(COD)Ir(μ-1κC^α:η^2-C≡$CSiMe_3$)(μ-2κC^α:η^2-C≡$CSiMe_3$)Pt(C_6F_5)$_2$]$^-$,[10] the influence of the metal centers in the M−C distances of the two η^2-coordinated C≡C triple bonds [Pt(1)−C(1) = 2.34(2) Å, Pt(1)−C(2) = 2.303(14) Å, Ir(1)−C(6) = 2.31(2) Å, Ir(1)−C(7) = 2.21(2) Å] as well as in both M−C σ-bonds [Pt(1)−C(6) = 1.99(2) Å, Ir(1)−C(1) = 2.00(2) Å] is insignificant. In accordance with the asymmetry found in the η^2-metal−acetylenic linkages where the M−C_β bond distances were slightly shorter than the corresponding M−C_α, the M−C_α≡C_β backbones remain almost linear [172.5(13)°, 179.2(13)°], while units C_α≡C_β−Si exhibit a marked deviation from linearity [147.4(13)°, 139.5(13)°]. The anion adopts a puckered shape, and the dihedral angle between the metal coordination planes is 144.1°. Similar nonplanar conformations have been found in [(COD)Ir(μ-C≡$CSiMe_3$)$_2$Pt(C_6F_5)$_2$]$^-$ [10] and in the symmetrical d^8−d^8 species [Ir(μ-C≡$CSiMe_3$)(COD)]$_2$[14] and [Pt(μ-C≡CPh)(C_6F_5)$_2$]$^{2-}$.[9a] However, in the neutral diplatinum complex [*trans*-Pt(μ-C≡CPh)(C_6F_5)(PPh_3)]$_2$,[9b] in early homobimetallic (d^1−d^1)[15] systems, and in some mixed species such us [Cp^2M(μ-1κC^α:η^2-C≡$CSiMe_3$)(μ-2κC^α:η^2-C≡$CSiMe_3$)Ni(PPh_3)] (M = Ti, Zr)[16] or [Cp^2Ti(μ-C≡C*t*-Bu)$_2$Pt(PPh_3)][17] the central MM′C_4 core is planar. In **1** the puckering does not result in any bonding metal interaction (Pt···Ir 3.538 Å).

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1·0.25CH$_2$Cl$_2$ and 4[a]

1·0.25CH$_2$Cl$_2$

Pt(1)−C(6)	1.99(2)	Pt(1)−C(16)	2.00(2)	Pt(1)−C(11)	2.01(2)
Pt(1)−C(1)	2.34(2)	Pt(1)−C(2)	2.303(14)	Pt(1)−Ir(1)	3.538
Ir(1)−C(1)	2.00(2)	Ir(1)−C(6)	2.31(2)	Ir(1)−C(7)	2.21(2)
Ir(1)−C(21)	2.21(2)	Ir(1)−C(22)	2.20(2)	Ir(1)−C(25)	2.11(2)
Ir(1)−C(26)	2.140(14)	C(1)−C(2)	1.27(2)	C(6)−C(7)	1.27(2)
C(11)−C(12)	1.23(2)	C(16)−C(17)	1.19(2)		

C(6)−Pt(1)−C(16)	89.0(6)	C(6)−Pt(1)−C(11)	179.1(6)
C(16)−Pt(1)−C(11)	90.1(6)	C(2)−C(1)−Ir(1)	172.5(13)
C(1)−C(2)−Si(1)	147.4(13)	C(7)−C(6)−Pt(1)	179.2(13)
C(6)−C(7)−Si(2)	139.5(13)	C(12)−C(11)−Pt(1)	178.2(14)
C(11)−C(12)−Si(3)	172(2)	C(17)−C(16)−Pt(1)	173.5(13)
C(16)−C(17)−Si(4)	175(2)	C(6)−Pt(1)−M(1)	79.82
C(11)−Pt(1)−M(1)	100.99	C(16)−Pt(1)−M(1)	167.79
M(3)−Ir(1)−M(4)	86.05	C(1)−Ir(1)−M(4)	175.26
M(2)−Ir(1)−M(3)	170.08	M(2)−Ir(1)−M(4)	103.43
M(2)−Ir(1)−C(1)	81.21	M(3)−Ir(1)−C(1)	89.36

4

Pt(1)−C(1)	1.967(9)	Pt(1)−C(6)	1.994(9)	Pt(1)−C(16)	2.005(9)
Pt(1)−C(12)	2.244(8)	Pt(1)−C(11)	2.377(8)	Pt(1)−Rh(1)	3.0034(8)
Ir(1)−C(11)	1.990(10)	Ir(1)−C(17)	2.204(10)	Ir(1)−C(16)	2.277(9)
Rh(1)−C(1)	2.274(8)	Rh(1)−C(6)	2.312(8)	Rh(1)−C(7)	2.424(9)
Rh(1)−C(2)	2.458(9)	C(1)−C(2)	1.212(12)	C(6)−C(7)	1.239(11)
C(11)−C(12)	1.248(12)	C(16)−C(17)	1.233(12)	Pt(1)−Ir(1)	3.611

C(1)−Pt(1)−C(6)	79.8(3)	C(1)−Pt(1)−C(16)	92.4(3)
C(6)−Pt(1)−M(5)	109.03	C(16)−Pt(1)−M(5)	78.72
C(2)−C(1)−Pt(1)	172.8(7)	C(7)−C(6)−Pt(1)	162.7(8)
C(17)−C(16)−Pt(1)	174.3(8)	C(12)−C(11)−Ir(1)	177.9(7)
C(1)−C(2)−Si(2)	165.2(8)	C(6)−C(7)−Si(1)	158.5(8)
C(11)−C(12)−Si(3)	150.3(7)	C(16)−C(17)−Si(4)	138.1(8)
M(1)−Rh(1)−M(2)	85.68	M(4)−Rh(1)−M(3)	86.40
M(1)−Rh(1)−M(3)	93.27	M(2)−Rh(1)−M(4)	97.14
M(7)−Ir(1)−M(8)	85.58	M(7)−Ir(1)−C(11)	88.82
M(6)−Ir(1)−M(8)	104.00	M(6)−Ir(1)−C(11)	81.58
Ir(1)−Pt(1)−Rh(1)	154.16		

[a] M(1) = midpoint between C(1) and C(2); M(2) = midpoint between C(6) and C(7); M(3) = midpoint between C(25) and C(26); M(4) = midpoint between C(21) and C(22); M(5) = midpoint between C(11) and C(12); M(6) = midpoint between C(16) and C(17); M(7) = midpoint between C(29) and C(30); M(8) = midpoint between C(33) and C(34).

Apart from the above considerations, all other distances and angles in the anion are within the expected ranges. In particular, the $C\equiv C$ bond lengths in the alkynyl bridging ligands are slightly longer [1.27(2) Å] than those observed for terminal groups [C(11)−C(12) 1.23(2), C(16)−C(17) 1.19(2) Å], and the Ir−(olefin) distances [range 2.11(2)−2.21(2) Å] are slightly asymmetric, the Ir−C bond *trans* to the $C\equiv C$ triple bond [2.11(2) Å, 2.140(14) Å] being shorter than the corresponding one *trans* to the sp C_α carbon donor [2.20(2) Å, 2.21(2) Å], consistent with the stronger *trans* influence of the σ-donor C_α carbon atom.[9b,10]

The crystal structure analysis of **4** (Figure 2, Table 1) clearly shows that despite the presence of an electrophilic cationic rhodium center [(COD)Rh]$^+$, no alkynylation process has taken place, but rather a simple complexation. In the final trimetallic complex, the "Rh(COD)" unit is stabilized by asymmetric [Rh−C_α 2.274(8), 2.312(8) Å; Rh−C_β 2.458(9), 2.424(9) Å] η^2-coordination of the rhodium atom to both alkynyl fragments of the binuclear anionic entity $[(COD)Ir(\mu\text{-}C\equiv CSiMe_3)_2Pt(C\equiv CSiMe_3)_2]^-$, yielding a very unusual polar (formally zwitterionic) trinuclear species. We have only previously observed the simultaneous presence of two different double-acetylide bridges, a σ/π and a chelating or tweezer type in the triplatinum complex $(NBu_4)_2[Pt_3(C_6F_5)_4(C\equiv CPh)_4]$.[11] However, complex **4** (as well as **3** and **5**) represents, to the best of our knowledge, the first trimetallic compound in which three different metals are linked together by double-alkynyl bridging systems. Furthermore, although there is a large number of complexes containing η^2-alkyne−rhodium bonds, the formation of species with a rhodium center η^2-bonded to two alkyne ligands is very rare.[8e,10,18] The synthesis of complexes such as **4** or **5**, where cationic rhodium or palladium $(Pd(\eta^3\text{-}C_3H_5)^+)$ atoms are unusually η^2-bonded to two alkyne entities, confirms the special ability of bis(alkynyl) metal building blocks to stabilize unusual organometallic entities. For instance, Lang et al.[4b] have proved elegantly that $[\{[Ti](C\equiv CR)_2\}Cu(CH_3)]$ (R = SiMe$_3$, *t*-Bu) exhibit a remarkably enhanced thermal stability when compared to the parent copper(I) methyl aggregate $[Cu(CH_3)]_n$. As can be observed in Figure 2, which shows a schematic view of the central core, the metal centers exhibit conventional square-planar environments and the whole anion is not planar. The dihedral angle formed by the best square-planar metal coordination planes around Pt(1) and Rh(1) is notably more acute (104.2°) than the corresponding one between Ir(1) and Pt(1) (157.7°), which is also reflected in the metal−metal separations, the Pt⋯Rh distance [3.0034(8) Å] being notably shorter than the Ir(1)⋯Pt(1) one (3.611 Å).

The η^2 interactions reflect not only the presence of different metals but also the different type of arrange-

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[18] (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press Ltd.: Oxford, U.K., 1982; Vol. 5. (b) *Comprehensive Organometallic Chemistry II*; Atwood, J. D., Vol. Ed.; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Elsevier: Oxford, U.K., 1995; Vol. 8.

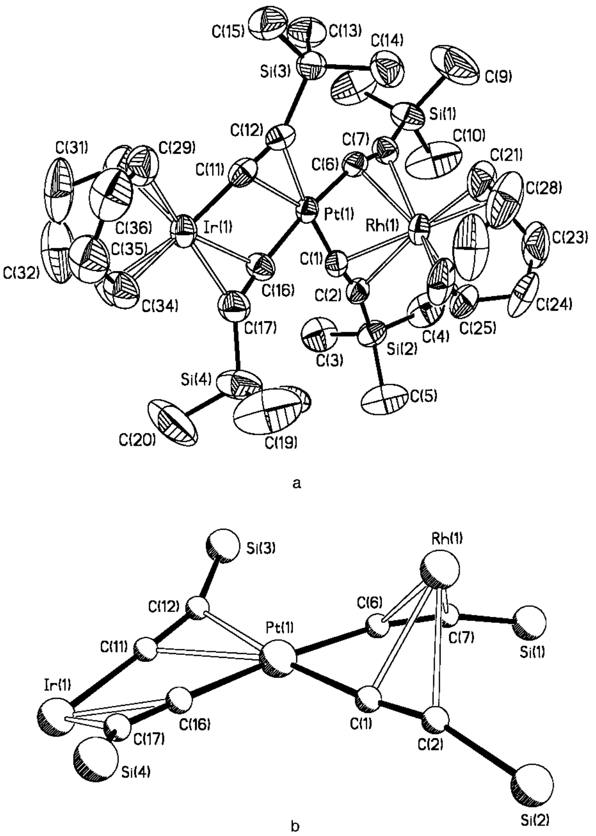


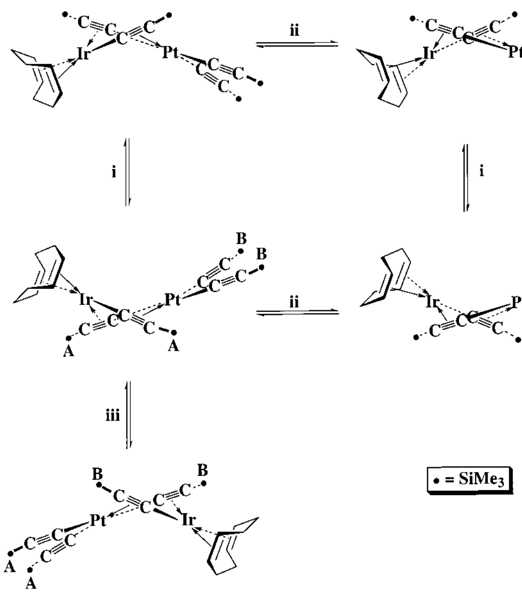
Figure 2. (a) View of the molecular structure of complex **4**, showing the atom-numbering scheme. Hydrogen atoms have been omitted for clarity. (b) Schematic view of the trimetallic central core of complex **4**.

ment for the alkynyl ligands. Thus, whereas the η^2-metal−acetylenic linkages in the IrC(11,12)C(16,17)Pt core exhibit the same asymmetry as that found in **1** (M−C_β bonds < M−C_α $\Delta = 0.13$ Å for Pt, 0.07 for Ir), the opposite asymmetry (Rh−C_α < Rh−C_β $\Delta = 0.184$, 0.112 Å) is observed in the Pt(1)C(1,2)C(6,7)Rh(1) organometallic framework. Accordingly, whereas both alkynyl ligands are only slightly bent at both C_α and C_β, respectively, in the chelating system [PtC_α≡C_β 172.8(7)°, 162.7(8)° and C_α≡C_β−Si 165.2(8)°, 158.5(8)°], they deviate significantly from 180° at C_β carbon atoms in the σ/π bridging system [angles at C_β C(11)−C(12)−Si(3) 150.3(7)°, C(16)−C(17)−Si(4) 138.1(8)° vs angles at C_α Ir(1)−C(11)−C(12) 177.9(7)° and Pt−C(16)−C(17) 174.3(8)°], as is usual for these systems. However, all C≡C triple bonds [range 1.212(12)−1.248(12) Å] are identical within experimental error. As expected, the η^2-coordination of both C≡CSiMe$_3$ triple bonds to the cationic rhodium atom Rh(1) reduces the bite angle C_α−Pt−C_α from 90.1(6)° in **1** to 79.8(3)° in **4**. However, the opposite angle is not influenced [C(6)−Pt(1)−C(2) 93.9(6)° in **1** vs C(16)−Pt(1)−C(12) 94.2(3)° in **4**].

(b) Spectroscopic Studies. Complexes **1**−**6** were characterized by usual analytical and spectroscopic methods. Conductivity measurements for anionic **1**−**3** species (see Experimental Section) are those expected for 1:1 electrolytes. In the case of complex **1** its IR spectrum strongly confirms not only the presence of bridging and terminal alkynyl ligands but also the activation of one σ Pt−C bond in the precursor [Pt(C≡CSiMe$_3$)$_4$]$^{2-}$. Thus, it shows two strong ν(C≡C) bands perceptibly shifted to lower wavenumbers (Δ 136 and 181 cm^{-1}) when compared with the precursor (1879, 1834 cm^{-1} in **1** vs 2015 cm^{-1} in [Pt(C≡CSiMe$_3$)$_4$]$^{2-}$), which is consistent with the formation of a σ/π double-alkynyl bridging system.[9a,b,d] We noted that smaller shifts may be expected for chelating or tweezer systems resulting from simple complexation processes.[8,9c,d] Further support of the alkynylation process comes from the fact that the ν(C≡C) bands, due to terminal alkynyl groups (2053(vs), 2034(vs) cm^{-1}), are notably shifted to higher frequencies. This fact is consistent with the decrease in the electron density at the Pt center in the final dimer, which reduces its π-back donor capability toward π* orbitals of the alkynyl ligands. As expected the IR spectra of the remaining complexes only exhibit ν(C≡C) absorptions in the range for carbon−carbon bonds coordinated to transition metal centers. As in precursor complex **1**, all compounds show four strong absorptions. The two low-frequency bands (∼1875−1884 cm^{-1}, 1840−1855 cm^{-1}), which appear at position similar to those observed in **1** are assigned to the σ/π bridging system (Ir−Pt) and the remaining two bands (1958−1986 cm^{-1}, 1927−1970 cm^{-1}) to the metalla-1,4-diyne chelating type (Pt−M, M = Pt **2**, Pd **3**, **5**, Rh **4**) or bridging (**6**) system. In particular, for compounds **2**−**5**, the moderate $\Delta\nu$(C≡C) shifts (67−107 cm^{-1}) relative to terminal alkynide groups in **1** are consistent with simple complexation of the ML$_n$ units via coordination to both alkynyl C≡C triple bonds, in agreement with the proposed structures.

Additional information is inferred from the NMR spectroscopy. Thus, the ^{13}C NMR spectrum of **1** at 289 K shows the expected resonances for four nonequivalent alkynyl ligands besides the olefinic and aliphatic carbon resonances of COD and the NBu$_4^+$ cation. However, the absence of platinum satellites at the eight quaternary C_α and C_β alkynyl carbons (δ 132.4−98.0) precludes a proper assignment. The presence of only two HC= (δ 78.16, 61.1) and CH$_2$ (δ 32.0, 31.7) resonances indicates the existence of a time-averaged plane of symmetry presumably caused by a very fast inversion of the central puckered bimetallacycle (i, Scheme 3). A comparable pattern exhibiting four SiMe$_3$ (δ 0.22, 0.19, −0.01, and −0.04) and two different HC= (δ 4.78(br), 3.50(br)) proton resonances is only observed at a low temperature (223 K) in the proton spectrum. Increasing the monitoring temperature resulted in a clear broadening of the olefinic resonances, which coalesce at about 273 K ($\Delta G^{\ddagger}_{273} = 12.2$ kcal·mol^{-1}) and finally collapse to a broad signal at 289 K (δ 4.18), and in the observation of only two types of alkynyl environments (terminal and bridging) above 243 K. A correlation ^{1}H-COSY spectrum at low temperature indicates that both olefinic signals are not coupled, confirming that they belong to protons with different C≡C bonds (*trans* to σ Ir−C and *trans* to π Ir−C$_2$). Therefore, the apparent C_{2v} symmetry observed at higher temperatures is explained by an additional σ/π intramolecular exchange of both alkynyl bridging groups (ii, Scheme 3) within the bimetallic framework, which seems to be rapid on the ^{1}H NMR chemical shift time scale at room temperature, but not on the ^{13}C NMR chemical shift time scale. The value of $\Delta G^{\ddagger}_{273}$ obtained is slightly higher than that previously

Scheme 3



observed for the related binuclear $(NBu_4)[(COD)Ir(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(C_6F_5)_2]$,[10] suggesting that the presence of electron-withdrawing C_6F_5 groups at the Pt center reduces the activation barrier. On raising the temperature, the olefinic resonance sharpens and both $SiMe_3$ resonances broaden; although coalescence is not reached at the highest accessible temperature (323 K), this further broadening of the alkynyl environments suggests the existence of a new dynamic process involving the exchange of the iridium entity between bridging and terminal alkynyl groups (iii, Scheme 3). At the same temperature the broadening is more extensive in acetone-d_6, pointing to the fact that this process is presumably favored in polar solvents.

Fluxional behavior for the remaining heterotrimetallic **2**−**5** and the hexanuclear species **6** is also evident. Due to the low solubility of complexes **2** and **3** in $CDCl_3$, their spectra were recorded in acetone-d_6. The scarce solubility of complex **2**, in this same solvent, precluded characterization by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of **3** at 223 K exhibits the characteristic signals for a rigid molecule with eight acetylenic and four $SiMe_3$ resonances from the alkynyl groups and the expected four olefinic and four aliphatic carbon signals of COD. It should be noted that, in this case, a possible fast inversion of the central puckered system IrC_4Pt (as observed in the solid state for **1** and **4**), which cannot be excluded, does not exchange the *endo* and *exo* halves of the COD group. The proton spectra of compounds **2** and **3** at room temperature look similar to that of the precursor **1**, exhibiting one olefinic signal (δ 4.30 **2**; 4.28 **3**) and two alkynyl environments (δ 0.24, 0.01 **2**; 0.24, 0.00 **3** $SiMe_3$) consistent with the existence of two mirror planes containing the metal centers on the bimetalla {Ir−Pt} unit. The observed pattern suggests the existence of a fast intramolecular exchange of the alkynyl groups with a simultaneous flipping of the "$M(C_6F_5)_2$" unit above and below the anionic bimetalla {Ir−Pt}-$(C{\equiv}CSiMe_3)_2$ entity or another dynamic process that equilibrates the *endo* and *exo* protons of the diolefin. In the two complexes, both the olefinic and the two $SiMe_3$ resonances broaden as the temperature is lowered, coalesce, and finally split. The HC= resonance coalesces in both species at ca. 263 K, but whereas for **2** it splits first into two different resonances clearly visible at 223 K (δ 4.90, ∼3.5) and, finally (183 K), into the four resonances expected in the low-exchange region, complex **3** gives rise to only two (δ 4.91, 3.83 at 223) even at the lower accessible limit (183 K). The comparison of the coalescent temperatures (∼273 K **1** vs 263 K **2** and **3**) seems to suggest that the π complexation of the neutral metal fragments "$M(C_6F_5)_2$" in **1** facilitates the intramolecular σ/π exchange of the alkynyl bridging ligands ($\Delta G^{\ddagger}_{263}$ ∼11.74 **2**, ∼ 11.72 **3** $kcal{\cdot}mol^{-1}$). In both complexes the low-frequency $SiMe_3$ signal is the first to split into two different signals [δ at 223 K 0.21 (18 H), −0.02 (9H), −0.06 (9 H) **2**; at 233 K 0.20 (18 H), −0.01 (9 H), −0.08 (9 H) **3**] and is, therefore, tentatively assigned to the nonequivalent trimethylsilyl protons of the frozen σ/π alkynyl bridging system. The high-frequency $SiMe_3$ resonance splits at lower temperatures: for **2** it is observed only at the lowest accessible limit [183 K δ 0.20 (9 H), 0.16 (9 H), −0.08 (br, 18 H)] and for **3** between 233 and 223 [223 K 0.21 (9 H), 0.19 (9H), −0.02 (9 H), −0.10(9 H)], and it is attributed to the tweezer system.

Along the same lines their ^{19}F NMR spectra are also temperature dependent (see Figure 3 for complex **3**). As can be seen for complex **3**, the pattern observed at low temperature (two different C_6F_5 rings with their halves nonequivalent) is that expected for a rigid molecule. In the *ortho* fluorine region the two signals located at high field have the appearance of triplets and are therefore attributed to *ortho* fluorine atoms of different rings.[19] Coupling between *ortho*-F atoms of different rings is rare but not unknown.[20] In our system, the attempts to confirm it by irradiation experiments on the *meta*-F signals at this low temperature were unsuccessful due to the separation of both *meta*-F resonances; but this scalar coupling through the space between two *ortho*-F of different rings was undoubtedly confirmed with a $^{19}F-^{19}F$ COSY spectrum (193 K, Figure 4). In this spectrum two less intense cross-peak signals were also observed, which led us to assign the signals at δ −107.10 and −111.47 (AK), as well as the signals at δ −109.25 and −110.69 (MX), as corresponding, respectively, to the two different C_6F_5 rings. Moreover, although no cross-peak signals are observed, the dynamic relation between the two signals located in the lower field, as well as that between the higher field resonances, is, as expected, clearly seen in the ^{19}F phase-sensitive NOESY spectrum at 193 K (Figure 5). This spectrum also shows less intense negative cross-peak signals between both groups of resonances which equilibrate, as commented below, at the highest available temperature (323 K). On raising the temperature (from 183 K), the *ortho* fluorine (*endo* with *endo* and *exo* with *exo* of both rings) and the *para* fluorine resonances broaden and collapse, giving rise to only one AA′MXX′

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[19] The appearance of the *ortho* region corresponding to an AKXM part of a complex eight-spin system (which also includes the *meta* fluorine atoms; AK *ortho*-F of one ring and XM *ortho*-F of the other ring) with $^4J_{ortho\text{-}F-ortho\text{-}F}$ in each ring ∼0, but with one strong inter-ring $^{19}F-^{19}F$ coupling (J_{AX} or $J_{KM} \neq 0$),[20] in addition to usual *ortho*-F−*meta*-F coupling.

[20] Alonso, M. A.; Casares, J. A.; Espinet, P.; Martínez-Ilarduya, J. M.; Pérez-Briso, C. *Eur. J. Inorg. Chem.* **1998**, 1745. (b) Albéniz, A. C.; Casado, A. L.; Espinet, P. *Organometallics* **1997**, *16*, 5416. (c) Espinet, P.; Gallego, A. M.; Martínez de Ilarduya, J. M.; Pastor, E. *Inorg. Chem.* **2000**, *39*, 975.

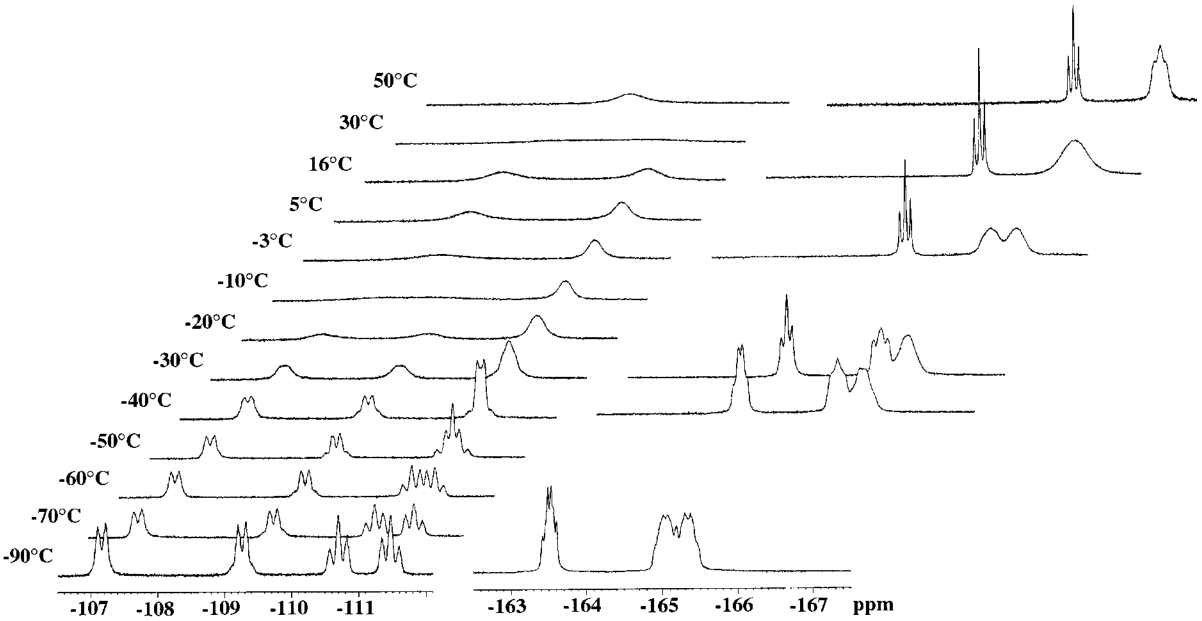

Figure 3. ^{19}F NMR spectra at different temperatures of complex **3** in acetone-d_6.

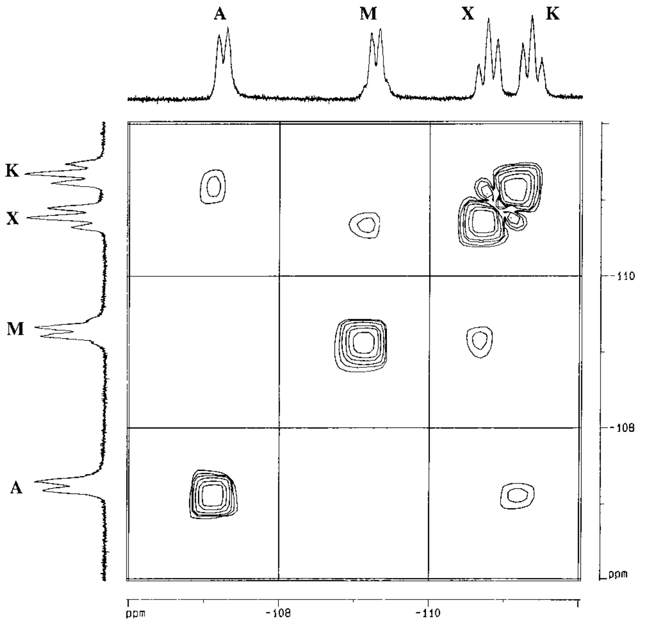

Figure 4. ^{19}F COSY spectrum (see ref 19 for the notation) of complex **3** in acetone-d_6 at 203 K (*ortho* fluoro region only).

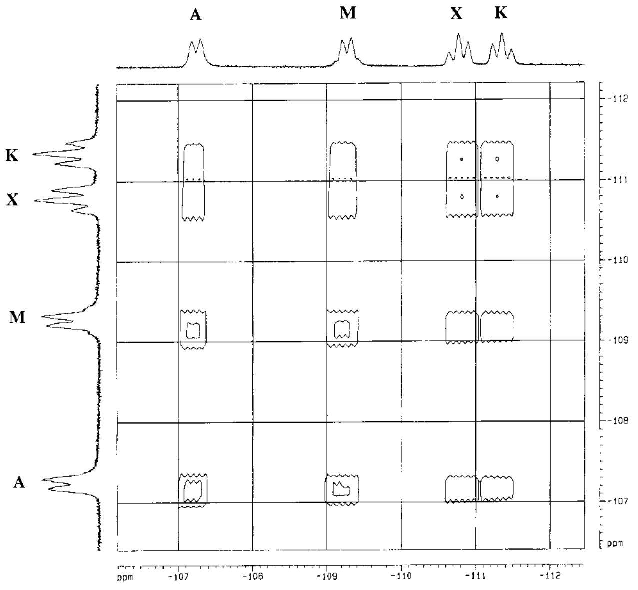

Figure 5. ^{19}F phase sensitive NOESY spectrum of complex **3** in acetone-d_6 at 203 K showing the negative cross-peaks (*ortho* fluoro region, notation according to ref 19).

spin system (one type of C_6F_5 ring) as a result of the fast σ/π intramolecular alkynyl migration between iridium and platinum atoms, which equilibrates both C_6F_5 groups. This process does not interconvert the *endo* and *exo* parts of the rings, and, therefore, the further equilibration observed above 303 K in the two *ortho* fluorine resonances requires the consideration of an additional dynamic process. A free rotation of the rings along the Pd−C bond or a facile flipping of the complexed $Pd(C_6F_5)_2$ unit above and below the planar anionic {Ir−Pt}$(C{\equiv}CSiMe_3)_2$ entity, or a combination of both processes, could adequately explain such changes. Similar behavior is observed for the heterotrimetallic Ir−Pt−Pt complex **2** (see Experimental Section for details).

The ^1H NMR spectra of the remaining complexes **4**−**6** in $CDCl_3$ at a low temperature (223 K) exhibit the expected separated signals for the COD and allyl groups present in a static situation. For complexes **4** and **5** assignments were made by $^1H-^1H$ COSY experiments. In complex **4** the small separation of the olefinic signals attributed to the COD ligand bound to Rh (δ 5.06(1H), 4.86, 4.55, and 4.47) vs the corresponding ones of the COD group bound to Ir (δ 5.06(1H), 4.93, 3.82, 3.63) as well as the chemical shift averages seen at higher temperatures (δ 4.75 Rh(COD) at room temperature and 4.41 Ir(COD) at 318 K) compares well with those previously reported for related complexes ([*cis*-$Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CSiMe_3)_2Rh(COD)]^-$ δ 4.78 (rt); [*cis*-$Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CSiMe_3)_2Ir(COD)]^-$ δ 4.27 (rt)).[10] However, the short range of temperatures in which the line-shape changes are detectable prevents us from taking this any further. For both complexes (**4** and **5**), only two different $SiMe_3$ resonances are observed even at 223 K. In contrast, the asymmetry of the ally group in **5** at low temperatures is in accord with the presence of five different signals [3.00(d), 3.17 (d) ($J_{anti} = 12.9$ Hz, 2 H_{anti}); 4.57(br), 4.66(br) (2H_{syn}); 5.38 (m, CH)] in the typical range.[21] The *syn* and *anti* protons together with the four olefinic signals of the COD broaden notably when the temperature is increased. The $HC=$ signals of the COD coalesce, giving rise to two very broad resonances at ca. 263 K (δ 5.00 and 3.65). These signals do not sharpen, but coalesce again at 289 K to a broad singlet, which sharpens at higher temperatures (δ 4.36 at 313 K). Averaging of the *anti*−*anti* and *syn*−*syn* protons of the allyl group is clearly visible above 263 K, giving rise to two sharp doublets at room temperature (δ 3.11, $J_{anti} = 12$ Hz; 4.55, $J_{syn} = 6$ Hz), but no averaging of the *syn* and *anti* signals is observed. Another significant observation in the ^{13}C NMR spectrum (assigned based on a DEPT experiment) of **5** at low temperatures is the existence of a total of four alkynyl environments (125.0−88.9, 8 C_α, C_β; 1.9−0.9 4 $SiMe_3$) and eight (4 $CH=$ and 4 CH_2, COD) and three (109.5 CH; 67.2, 66.4 CH_2; allyl) characteristic carbon resonances for the COD and allyl groups, respectively, consistent with the formulation shown in Scheme 2.

The hexametallic $[(\eta^2\text{-}\{Ir-Pt\}(C\equiv CSiMe_3)_2)_2Ag_2]$ (**6**) is not soluble enough for a ^{13}C NMR study, but its proton spectrum in $CDCl_3$ at low temperatures shows the expected four olefinic and four alkynyl environments. This complex is also dynamic, and in the fast regime-exchange at 303 K (see Experimental Section for details) only one olefinic resonance and two $SiMe_3$ signals are found (at higher temperatures considerable decomposition is observed) consistent with the existence of mirror planes containing the iridium and platinum atoms on the $\{Ir-Pt\}(C\equiv CSiMe_3)_2$ entities.

In conclusion, we have investigated the reactivity of the homoleptic species $[Pt(C\equiv CR)_4]^{2-}$ toward the electrophilic building block $[Ir(COD)]^+$. We have found that only the compound with R = $SiMe_3$ is a suitable precursor and that the reaction evolves yielding a very stable anionic heterobimetallic complex **1**, stabilized by a σ/π double-alkynide bridging system, which is formed by a σ alkynyl migration process from Pt to Ir (X-ray). Formation of a symmetric (through a further alkynylation) or asymmetric (by simple π complexation) trimetallic Ir−Pt−Ir compound could not be achieved. However, the coordination ability of the heterobimetallic tweezer complex $(NBu_4)\{Ir-Pt\}(C\equiv CSiMe_3)_2$ (**1**), which still contains two mutually *cis* alkynyl ligands, has been used successfully to synthesize heterotrimetallic anionic $[\{Ir-Pt\}(\mu\text{-}2\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)_2M(C_6F_5)_2]^-$ (M = Pt **2**, Pd **3**) or neutral $[\{Ir-Pt^-\}(\mu\text{-}2\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)_2M^+L_n]$ (ML_n = Rh(COD) **4** and Pd(η^3-C_3H_5) **5**) species. The structure of $[\{Ir-Pt^-\}(\mu\text{-}2\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)_2Rh^+(COD)]$ (**4**), which confirms the formally zwitterionic nature of these neutral species, has been solved by an X-ray diffraction study, and to our knowledge this is the first report of a heterotrimetallic complex stabilized by double-alkynide bridges. The construction of an unusual hexametallic $\{Ir-Pt\}_2Ag_2$ compound **6** is also achieved by a neutralization process with 1 equiv of $AgClO_4$. NMR spectroscopy confirms, as is usual for many alkynyl bridging complexes, that all these compounds have a dynamic behavior in solution.

Experimental Section

General methods and instrumentation have been described previously.[10] All coupling constants are given in hertz. Homonuclear correlation NMR spectra ($^1H-^1H$ and $^{19}F-^{19}F$) and ^{19}F phase-sensitive NOESY spectra were recorded on a Bruker ARX 300. $(NBu_4)_2[Pt(C\equiv CSiMe_3)_2]\cdot 2H_2O$,[11] [*cis*-$Pt(C_6F_5)_2(THF)_2$] (M = Pd, Pt),[22] $[M(\mu\text{-}Cl)(COD)]_2$ (M = Rh,[23a] Ir[23b]), and $AgClO4$[24] were prepared by published methods.

Preparation of $(NBu_4)[(COD)Ir(\mu\text{-}1\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)(\mu\text{-}2\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)Pt(C\equiv CSiMe_3)_2]$ (1). A suspension of $[Ir(\mu\text{-}Cl)(COD)]_2$ (0.09 g, 0.13 mmol) in acetone (5 mL) at 263 K was treated with $(NBu_4)_2[Pt(C\equiv CSiMe_3)_4]\cdot 2H_2O$ (0.30 g, 0.27 mmol), and the mixture was stirred for 8 min. From the resulting yellow suspension complex **1** was filtered as a yellow solid (52% yield).

Complex **1** was also obtained in a 51% yield following the same procedure, but starting from 0.20 g (0.30 mmol) of $[Ir(\mu\text{-}Cl)(COD)]_2$ and 0.33 g (0.30 mmol) of $(NBu_4)_2[Pt(C\equiv CSiMe_3)_4]\cdot 2H_2O$ (Ir/Pt molar ratio 2:1).

Complex **1** can also be obtained in a very low yield (19%) by treatment of 0.15 g (0.14 mmol) of $(NBu_4)_2[Pt(C\equiv CSiMe_3)_4]\cdot 2H_2O$ with a solution of $[Ir(COD)(acetone)_x](ClO_4)$ (Ir/Pt molar ratio 2:1), prepared with 0.10 g (0.15 mmol) of $[Ir(\mu\text{-}Cl)(COD)]_2$ and 0.06 g (0.29 mmol) of $AgClO_4$ and 1 h of stirring, in 20 mL of acetone. Evaporation to dryness of the resulting orange solution and treatment of the solid residue with cold EtOH (~5 mL) yielded 0.03 g of **1**. Anal. Calcd for $C_{44}H_{84}IrNPtSi_4$: C, 46.9; H, 7.5; N, 1.2. Found: C, 46.7; H, 7.4; N, 1.0. Λ_M: 68 Ω^{-1} cm^2 mol^{-1}. MS FAB(−): *m/z* 884 $[M]^-$ 100%; 777 [M − COD + 2] 36%; 690 [M − 2 C_2SiMe_3 + 1] 47%; 486 $[Pt(C_2SiMe_3)_3]$ 43%; 389 $[Pt(C_2SiMe_3)_2]$ 26%. IR (cm^{-1}): $\nu(C\equiv C)$ 2053(vs), 2034(vs), 1879(vs), 1834(vs). ^1H NMR ($CDCl_3$, δ): at 298 K, 4.18 (s br, $CH=$, COD, 4H); 3.43 (s br, $N-CH_2-$, NBu_4, 8H); 2.09 (s br, $CH_2<$, COD, 4H); 1.91 (m, $CH_2<$, COD, 4H), 1.68 (s br, $-CH_2-$, NBu_4, 8H); 1.49 (m, $-CH_2-$, NBu_4, 8H); 1.00 (t, $-CH_3$, NBu_4, 12H); 0.26 (s, $SiMe_3$, 18H); 0.03 (s, $SiMe_3$, 18H). At 223 K, 4.78 (s br, $CH=$, COD, 2H); 3.50 (s br, $CH=$, COD, 2H); 3.37 (s br, $N-CH_2-$, NBu_4, 8H); 2.10 (s br, $CH_2<$, COD, 2H); 1.99 (s br, $CH_2<$, COD, 4H); 1.86 (s br, $CH_2<$, COD, 2H); 1.61 (s br, $-CH_2-$, NBu_4, 8H); 1.45 (s br, $-CH_2-$, NBu_4, 8H); 0.96 (s br, $-CH_3$, NBu_4, 12H); 0.22 (s, $SiMe_3$, 9H); 0.19 (s, $SiMe_3$, 9H); −0.01 (s, $SiMe_3$, 9H); −0.04 (s, $SiMe_3$, 9H). The signal due to the olefinic protons of the COD coalesces at ~273 K ($\Delta G_{273}^{\ddagger} = 12.25$ kcal·mol^{-1}). ^{13}C NMR ($CDCl_3$, δ): at 289 K, 132.4(s), 128.0(s), 119.5(s), 112.0(s), 117.4(s), 109.9(s), 109.6 (s), 98.0(s) (C_α, C_β); 78.6(br, $CH=$, COD); 61.1(s, $CH=$, COD); 58.1(s, $N-CH_2-$, NBu_4); 32.0(s, $CH_2<$, COD); 31.7(s, $CH_2<$, COD); 24.0(s, $-CH_2-$, NBu_4); 19.7(s, $-CH_2-$, NBu_4); 14.0(s, $-CH_3$, NBu_4); 2.2(s, $SiMe_3$); 1.8(s, $SiMe_3$); 1.4(s, $SiMe_3$); 1.3(s, $SiMe_3$).

Preparation of $(NBu_4)[(COD)Ir(\mu\text{-}1\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)(\mu\text{-}2\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)Pt(\mu\text{-}2\kappa C^{\alpha}:\eta^2\text{-}C\equiv CSiMe_3)_2M(C_6F_5)_2]$ (M = Pt 2, Pd 3). A solution of **1** (0.15 g, 0.13 mmol) in 20 mL of CH_2Cl_2 at 253 K was treated with 0.09 g (0.13 mmol) of [*cis*-$Pt(C_6F_5)_2(THF)_2$], and the resulting orange solution was immediately evaporated to dryness. Treatment of the residue with cold Et_2O (~5 mL) afforded complex **2** (M = Pt) as a yellow solid (yield 41%).

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[21] The presence of two different rotamers in equal proportion, and dynamic on the NMR time scale, cannot be totally excluded.

[22] Usón, R.; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* **1985**, *4*, 1912.

[23] (a) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88. (b) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

[24] Smith, G. F.; Ring, J. *J. Am. Chem. Soc.* **1937**, *59*, 1889.

Complex **3** (M = Pd) can be obtained as a yellow solid as previously described, starting from 0.15 g (0.13 mmol) of **1** and 0.08 g (0.13 mmol) of [*cis*-Pd(C$_6$F$_5$)$_2$(THF)$_2$] (yield 43%).

Data for 2. Anal. Calcd for C$_{56}$H$_{84}$F$_{10}$IrNPt$_2$Si$_4$: C, 40.6; H, 5.1; N, 0.9. Found: C, 40.2; H, 5.3; N, 0.9. Λ_M: 117 Ω^{-1} cm^2 mol^{-1}. MS ES(−): *m/z* 1414 [M + 1]$^-$ 73%. IR (cm^{-1}): ν(C≡C) 1958(s), 1927(s), 1881(s), 1844(s); ν(C$_6$F$_5$) 800(s), 788(s). ^{1}H NMR (acetone-d_6, δ): at 289 K, 4.30(s br, CH=, COD, 4H); 3.46(t, N−CH$_2$-, NBu$_4$, 8H); 2.85(m br, CH$_2$<, COD, 4H); 1.94(m, CH$_2$<, COD, 4H), 1.84(m, −CH$_2$−, NBu$_4$, 8H); 1.44(m, −CH$_2$−, NBu$_4$, 8H); 0.98(t, −CH$_3$, NBu$_4$, 12H); 0.24(s, SiMe$_3$, 18H); 0.01(s, SiMe$_3$, 18H). The olefinic resonance disappears at ca. 263 K, first splitting into two broad resonances, which are clearly visible at 223 K (δ 4.90, 2H; ~3.5 2H, this signal overlaps with the resonance at 3.41 ppm of the N−CH$_2$ protons) and, finally, into four different signals at 183 K (δ 4.86; 4.78; 3.61; ~3.4, this signal overlaps with the N−CH$_2$ protons). The SiMe$_3$ signals also broaden and split. The SiMe$_3$ low-frequency resonance clearly splits between 233 and 223 K (δ at 223 K 0.21(18H), −0.02(9H), −0.06(9H)), but probably due to bad resolution (broad signals), the high-frequency resonance is only observed to split at 183 K (δ 0.20 (9H), 0.16(9H), −0.08(br, 18H). ^{19}F NMR (acetone-d_6, δ): at 289 K, −113.27(d, $^3J_{\mathrm{Pt}-ortho-\mathrm{F}}$ = 440, 4*ortho*-F); −166.98(t, 2*para*-F); −167.55(m, 4*meta*-F). At 193 K, −111.93(d, 1*ortho*-F); −112.14(pt, 1*ortho*-F); −113.96(d, 1*ortho*-F); −114.50(pt, 1*ortho*-F); −165.14, −165.19 (two triplets overlapped, 2*para*-F); −166.08(m, 4*meta*-F). Above 203 K only one *para*-F is observed. In the *ortho*-F region the two pseudotriplet signals approximate on heating and coalesce to only one broad singlet at 233 K (δ −113.35), while the two doublets also broaden, but their coalescence temperature (243 to 253 K) is not clear. At 263 K only a broad singlet (δ −113.34, 4F) with Pt satellites is seen, which sharpens at higher temperatures. The low solubility of this complex precluded its characterization by ^{13}C NMR spectroscopy.

Data for 3. Anal. Calcd for C$_{56}$H$_{84}$F$_{10}$IrNPdPtSi$_4$: C, 42.9; H, 5.4; N, 0.9. Found: C, 42.6; H, 5.1; N, 1.2. Λ_M: 103 Ω^{-1} cm^2 mol^{-1}. MS ES(−): *m/z* 1327 [M + 2]$^-$ 100%. IR (cm^{-1}): ν(C≡C) 1986(s), 1957(s), 1881(s), 1845(s); ν(C$_6$F$_5$) 786(s), 774(s). ^{1}H NMR (acetone-d_6, δ): at 289 K, 4.28(br, CH=, COD, 4H); 3.47(t, N−CH$_2$−, NBu$_4$, 8H); 2.19(m, CH$_2$<, COD, 4H); 1.96(m, CH$_2$<, COD, 4H); 1.84(m, −CH$_2$−, NBu$_4$, 8H); 1.44(m, −CH$_2$−, NBu$_4$, 8H); 0.98(t, −CH$_3$, NBu$_4$, 12H); 0.24(s, SiMe$_3$, 18H); 0.00(s, SiMe$_3$, 18H). On cooling, the =CH signal disappears at ca. 263 K and splits in two resonances. The SiMe$_3$ resonances also broaden and split: the low-frequency signal splits between 243 and 233 K and the high frequency between 233 and 223 K. At 223 K, 4.91(br, CH=, COD, 2H); 3.83(m, CH=, COD and N−CH$_2$−, NBu$_4$, 10H); 2.14−1.90(CH$_2$<, COD, 8H); 1.88(m, −CH$_2$−, NBu$_4$, 8H); 1.30(m, −CH$_2$−, NBu$_4$, 8H); 0.93(t, −CH$_3$, NBu$_4$, 12H); 0.21(s, SiMe$_3$, 9H); 0.19(s, SiMe$_3$, 9H); −0.02(s, SiMe$_3$, 9H); −0.1(s, SiMe$_3$, 9H). $\Delta G^{\ddagger}_{263}$ (using the ΔHz for HC= at 183 K) = 11.72 kcal·mol^{-1}. ^{19}F NMR (acetone-d_6, δ): see Figure 3 for spectrum at different temperatures. At 323 K, −109.59(br, 4*ortho*-F); −165.82(t, 2*para*-F); −166.99(m, 4*meta*-F); ($T_{\mathrm{coalescence}}$ for *ortho*-F ca. 303 K). At 289 K, −108.49(br, 2*ortho*-F); −110.73(br, 2*ortho*-F); −165.33(t, 2*para*-F); −166.62(m, 4*meta*-F). All signals broaden on cooling and finally split at lower temperatures; below 233 K two *para*-F resonances are observed. At 183 K, −107.10(d, 1*ortho*-F); −109.25(d, 1*ortho*-F); −110.69(pt, 1*ortho*-F); −111.47(pt, 1*ortho*-F); −163.41(t, 1*para*-F); −163.52(t, 1*para*-F); −165.03(m), −165.33(m, 4*meta*-F). Whereas the two high-field *ortho*-F signals strongly approximate on heating yielding a broad singlet at 243 K (δ −110.93), the two low-field *ortho*-F signals only broaden and coalesce at higher temperatures (between 263 and 270 K). ^{13}C NMR (acetone-d_6, δ): at 223 K, 148.3−134.0 (C$_6$F$_5$); 124.8(s), 122.3(s), 120.3(s), 119.0(s), 109.9(s), 108.1(s), 104.0 (s), 91.8(s) (C$_\alpha$, C$_\beta$); 78.8(s), 77.8(s), 62.9(s), 62.6(s) (CH=, COD); 58.4(s, N−CH$_2$−, NBu$_4$); 32.7(s), 32.2(s), 32.1(s), 31.4(s) (CH$_2$<, COD); 23.8(s, −CH$_2$−, NBu$_4$); 20.0(s, −CH$_2$−, NBu$_4$); 13.9(s, −CH$_3$, NBu$_4$); 1.8(s, SiMe$_3$); 1.3(s, SiMe$_3$); 0.5(s, 2SiMe$_3$).

Preparation of [(COD)Ir(μ-1κC^{α}:η^2-C≡CSiMe$_3$)(μ-2κC^{α}:η^2-C≡CSiMe$_3$)Pt(μ-2κC^{α}:η^2-C≡CSiMe$_3$)$_2$Rh(COD)] (4). A yellow solution of [Rh(μ-Cl)(COD)]$_2$ (0.035 g, 0.07 mmol) in acetone (20 mL) was treated with AgClO$_4$ (0.03 g, 0.14 mmol), and the mixture was stirred for 1 h at room temperature and then filtered through Kieselgurh. The resulting yellow solution, which contains [Rh(COD)(acetone)$_2$](ClO$_4$), was evaporated to ca. 5 mL, cooled to 263 K, and then treated with 0.15 g (0.13 mmol) of **1** to give a red solution, which was evaporated to dryness. Treatment of the resulting residue with 5 mL of cold EtOH afforded **4** as an orange solid (65% yield). Anal. Calcd for C$_{36}$H$_{60}$IrPtRhSi$_4$: C, 39.5; H, 5.5. Found: C, 39.2; H, 5.5. MS FAB(+): *m/z* 1095 [M]$^+$ 49%; 699 [Pt(C$_2$SiMe$_3$)$_3$Rh(COD) + 2]$^+$ 100%. IR (cm^{-1}): ν(C≡C) 1986(s), 1953(s), 1875(s), 1844(s). ^{1}H NMR (CDCl$_3$, δ): at 298 K, 4.75 (s br, CH=, COD, Rh, 4H); 4.46(br), 4.33(br) (CH=, COD, Ir, 4H; these signals coalesce over 303 K to give at 318 K a broad signal at 4.41 ppm); 2.41(s br, CH$_2$<, COD, Ir, 4H); 2.22 (m, CH$_2$<, COD, Rh, 4H); 2.00 (m, CH$_2$<, COD, Rh, 4H); 1.86(m, CH$_2$<, COD, Ir, 4H); 0.26 (s, SiMe$_3$, Ir, 18H); 0.20 (s, SiMe$_3$, Rh, 18H). At 223 K, 5.06 (s br, CH=, COD, Rh, Ir, 2H); 4.93 (s br, CH=, COD, Ir, 1H); 4.86 (s br, CH=, COD, Rh, 1H); 4.55 (s br, CH=, COD, Rh, 1H); 4.47 (s br, CH=, COD, Rh, 1H); 3.82 (s br, CH=, COD, Ir, 1H); 3.63 (s br, CH=, COD, Ir, 1H); 2.45(s br, CH$_2$<, COD, Ir, 2H); 2.29(s br, CH$_2$<, COD, Rh, 2H); 2.21(s br, CH$_2$<, COD, Rh, 4H); 2.13(s br, CH$_2$<, COD, Ir, 2H); 1.93(s br, CH$_2$<, COD, Ir, 4H); 1.73(s br, CH$_2$<, COD, Rh, 2H); 0.22(s, SiMe$_3$, Rh, 18H); 0.17(s, SiMe$_3$, Ir, 18H; this signal finally split in two singlets at 0.18 and 0.17 ppm at 213 K). ^{1}H NMR spectra were assigned on the basis of ^{1}H−^{1}H COSY NMR spectra. ^{13}C NMR (CDCl$_3$, δ): at 289 K, 126.5(s), 123.8(s) (C$_\alpha$ or C$_\beta$); 80.6(d, $^1J_{\mathrm{Rh-C}}$ = 13, CH=, COD); 71.8(br, CH=, COD); 31.8(s, CH$_2$<, COD); 31.2(s, CH$_2$<, COD); 1.8(s, SiMe$_3$), 1.3(s, SiMe$_3$).

Preparation of [(COD)Ir(μ-1κC^{α}:η^2-C≡CSiMe$_3$)(μ-2κC^{α}:η^2-C≡CSiMe$_3$)Pt(μ-2κC^{α}:η^2-C≡CSiMe$_3$)$_2$Pd(η^3-C$_3$H$_5$)] (5). A suspension of 0.35 g (0.31 mmol) of **1** in 20 mL of acetone at 253 K was treated with 0.6 g (0.16 mmol) of [Pd(η^3-C$_3$H$_5$)(μ-Cl)]$_2$ and 0.3 g (2.45 mmol) of NaClO$_4$ to give immediately an orange solution, which was evaporated to dryness. The residue was extracted with 40 mL of Et$_2$O, filtered through Kieselgurh, and evaporated to dryness. Treatment of the residue with deoxygenated water afforded complex **5** as a yellow solid (yield 57%). Anal. Calcd for C$_{31}$H$_{53}$IrPdPtSi$_4$: C, 36.1; H, 5.2. Found: C, 36.1; H, 5.1. MS FAB(+): *m/z* 990 [M − C$_3$H$_5$]$^+$ 26%. IR (cm^{-1}): ν(C≡C) 1973(vs), 1954(s), 1880(s), 1840(s). ^{1}H NMR (CDCl$_3$, δ): at 289 K, 5.36(m, CH, allyl, 1H), 4.55(d, J_{syn} = 6, CH$_2$, allyl, 2H$_{syn}$); 3.11(d, J_{anti} = 12, CH$_2$, allyl, 2H$_{anti}$); 2.20(m, CH$_2$<, COD, 4H); 1.97(m, CH$_2$<, COD, 4H); 0.27(s, SiMe$_3$, 18H); 0.15(s, SiMe$_3$, 18H) (CH= protons of COD appear as a very broad signal that almost coincides with the baseline, centered at δ ~4.30; this signal is also observed on the diagonal of the ^{1}H−^{1}H COSY spectrum at 289 K and sharpens on heating to 313 K to give a broad singlet at 4.36 ppm). At 223 K, 5.38(m, CH, allyl, 1H), 5.16 (s br, CH=, COD, 1H); 4.97 (s br, CH=, COD, 1H); 4.66(s br, CH$_2$, allyl, 1H$_{syn}$); 4.57(s br, CH$_2$, allyl, 1H$_{syn}$); 3.87 (s br, CH=, COD, 1H); 3.52 (s br, CH=, COD, 1H); 3.17(d, J_{anti} = 9, CH$_2$, allyl, 1H$_{anti}$); 3.00(d, J_{anti} = 12, CH$_2$, allyl, 1H$_{anti}$); 2.20(br, CH$_2$<, COD, 6H); 1.79(m, CH$_2$<, COD, 2H); 0.27(s, SiMe$_3$, 18H); 0.13(s, SiMe$_3$, 18H). The four olefinic signals of COD coalesce giving two very broad resonances at ca. 263 K (δ 5.00 and 3.65) but do not sharpen. They coalesce again at 289 K. ^{13}C NMR (CDCl$_3$, δ): at 223 K, 125.0(s), 120.0(s), 118.0(s) (C$_\alpha$, C$_\beta$); 109.5(s, CH, allyl); 109.4(s), 108.2(s), 99.6(s), 98.0(s), 88.9(s) (C$_\alpha$, C$_\beta$); 81.6(s, CH=, COD); 79.3(s, CH=, COD); 67.2(s, CH$_2$, allyl); 66.4(s, CH$_2$, allyl); 63.7(s, CH=, COD); 63.6(s, CH=, COD); 33.4(s, CH$_2$<, COD); 32.7(s, CH$_2$<, COD); 30.5(s, CH$_2$<, COD); 30.0(s, CH$_2$<, COD); 1.9(s, SiMe$_3$);

Table 2. Crystal Data and Structure Refinement Parameters for 1·0.25CH$_2$Cl$_2$ and 4

	1·0.25CH$_2$Cl$_2$	**4**
empirical formula	C$_{44.25}$H$_{84.5}$Cl$_{0.5}$IrNPtSi$_4$	C$_{36}$H$_{60}$IrPtRhSi$_4$
fw	1148.00	1095.40
temperature, K	250(2)	200(2)
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*
a, Å	14.724(2)	15.788(3)
b, Å	16.752(4)	17.668(3)
c, Å	23.030(2)	16.229(3)
α, deg	90	90
β, deg	94.70(1)	104.47(2)
γ, deg	90	90
volume, Å^3	5661(2)	4383.4(14)
Z	4	4
density(calcd), Mg/m^3	1.347	1.660
abs coeff, mm^{-1}	4.950	6.715
F(000)	2306	2128
cryst size, mm	0.58 × 0.16 × 0.14	0.54 × 0.18 × 0.10
θ range for data collection, deg	2.10 to 24.00	2.31 to 26
index ranges	$0 \leq h \leq 16$, $-19 \leq k \leq 3$, $-26 \leq l \leq 26$	$-19 \leq h \leq 3$ $-21 \leq k \leq 3$ $-19 \leq l \leq 20$
no. of reflns colld	10 089	9111
no. of ind reflns	8811 [*R*(int) = 0.0947]	8581 [*R*(int) = 0.0410]
refinement method	full-matrix least-squares on F^2	
no. of data/restraints/params	7410/3/460	7868/0/376
goodness-of-fit on F^2 [a]	1.039	1.036
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0625, wR2 = 0.1222	R1 = 0.0449, wR2 = 0.0959
R indices (all data)[a]	R1 = 0.1472, wR2 = 0.1793	R1 = 0.0755, wR2 = 0.1101
largest diff peak and hole, e Å^{-3}	0.878 and −0.901	0.840 and −0.754

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$; goodness of fit $= \sum w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]$; $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2;0 + 2F_c^2]/3$.

1.3(s, SiMe$_3$); 1.1(s, SiMe$_3$); 0.9(s, SiMe$_3$). Assignment based on a ^{13}C DEPT spectrum.

Preparation of [{(COD)Ir(μ-1κC^{α}:η^2-C≡CSiMe$_3$)(μ-2κC^{α}:η^2-C≡CSiMe$_3$)Pt(μ-2κC^{α}:η^2-C≡CSiMe$_3$)$_2$}Ag]$_2$ (6). A 0.21 g (0.18 mmol) sample of **1** was added to a solution of 0.038 g (0.18 mmol) of AgClO$_4$ in 20 mL of acetone at 253 K, and the resulting orange suspension was stirred for 30 min. Evaporation of the mixture to ca. 5 mL caused the precipitation of **6** as a deep orange solid, which was filtered and washed with 5 mL of cold EtOH (Yield 67%). Anal. Calcd for Ag$_2$C$_{56}$H$_{96}$Ir$_2$Pt$_2$Si$_8$: C, 33.9; H, 4.9. Found: C, 34.1; H, 5.0. MS ES(−): *m*/*z* 1415 (26%); 1118 (100%). IR (cm^{-1}): ν(C≡C) 1985(vs), 1970(s), 1884(s), 1855(s). ^{1}H NMR (CDCl$_3$, δ): at 289 K, 2.16(s br, CH$_2$<, COD, 8H); 1.97(m, CH$_2$<, COD, 8H); 0.26(s, SiMe$_3$, 36H); 0.22(s, SiMe$_3$, 36H). At 223 K, 5.12 (s br, CH=, COD, 2H); 4.73 (s br, CH=, COD, 2H); 3.91 (s br, CH=, COD, 2H); 3.39 (s br, CH=, COD, 2H); 2.21(br, CH$_2$<, COD, 4H); 2.09(br, CH$_2$<, COD, 8H); 1.76(br, CH$_2$<, COD, 4H); 0.23(s, SiMe$_3$, 18H); 0.19(s, SiMe$_3$, 36H); 0.17(s, SiMe$_3$, 18H). The four signals due to CH= protons of COD coalesce between 243 and 253 K to give two very broad signals that almost coincide with the baseline (δ at 253 K ~4.90 and 3.70). These two signals do not sharpen, but they coalesce again between 273 and 289 K to give again a unique very broad resonance centered at ~4.30 ppm, which sharpens on heating (δ at 313 K 4.37(br)). Due to the low solubility of this complex, the ^{13}C NMR spectra could not be done.

X-ray Crystallographic Analysis of 1·0.25CH$_2$Cl$_2$ and 4. Crystals of both complexes were obtained at a low temperature (243 K) by slow diffusion of hexane into dichlorometane solutions. Table 2reports details of the structure analyses for **1**·0.25CH$_2$Cl$_2$ and **4**.

Selected crystals of complexes **1**·0.25CH$_2$Cl$_2$ and **4** were fixed with epoxy on top of a glass fiber and transferred to the cold stream of the low-temperature device of an automated four-circle difractometer Siemens P4. Cell constants were calculated from 23 well-centered reflections with 2θ angles ranging from 23° to 25° (**1**·0.25CH$_2$Cl$_2$) or from 24° to 26° (**4**). Data were collected by the θ/2θ method. Three check reflections measured at regular intervals showed a loss of intensity of 20% at the end of data collection for **1**·0.25CH$_2$Cl$_2$, while no significant loss of intensity was detected for **4**. An empirical absorption correction based on ψ scans was applied (16 reflections, maximum and minimum transmission factors = 0.977 and 0.697 for **1**·0.25CH$_2$Cl$_2$; 12 relections, maximum and minimum transmission factors = 1.000 and 0.619 for **4**). The structures were solved by the Patterson method. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and assigned isotropic displacement parameters equal to 1.2 or 1.5 times the U_{iso} value of their respective parent carbon atoms. For complex **1**, regions of electron density located at nonbonding distances were modeled as interstitial CH$_2$Cl$_2$ (a quarter of a molecule of solvent per formula unit) and refined with isotropic displacement parameters. There is no residual electronic density higher than 1 e/A^3 in the final maps. All calculations were carried out using the program SHELXL-93.[25]

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Supporting Information Available: X-ray crystallographic data in CIF format for **1**·0.25CH$_2$Cl$_2$ and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010097D

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[25] Sheldrick, G. M. *SHELXL-93, FORTRAN 77 Program for Crystal Structure Determination from Diffraction Data*; University of Göttingen: Germany, 1993.