$[Pt(C{\equiv}CR)_4]^{2-}$ as Double Alkynylation Reagents: Facile Formation of Binuclear Bis(μ-alkynide) (M−Pt) and Unsymmetrical Trinuclear Double Bis(μ-alkynide) (M−Pt−Pt) Complexes

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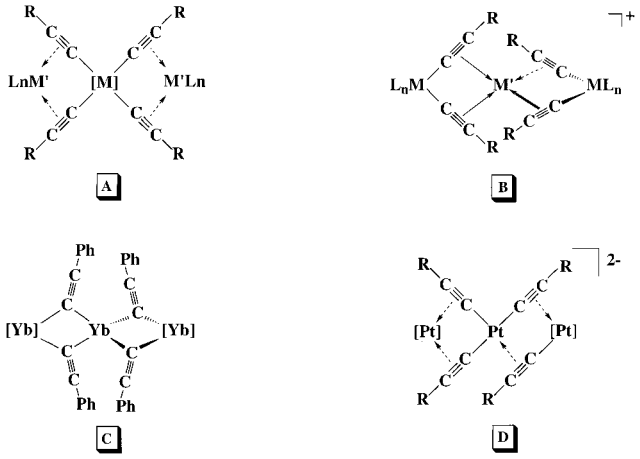
Treatment of $(NBu_4)_2[Pt(C{\equiv}CR)_4]\cdot 2H_2O$ (R = *t*-Bu, **1a**; $SiMe_3$, **1b**; Ph, **1c**) with 1 equiv of the dicationic solvento species $[Cp^*M(PEt_3)(acetone)_2](ClO_4)_2$ (M = Rh, Ir) results in double alkynyl transfer to give the binuclear compounds $[(PEt_3)Cp^*M(\mu\text{-}1\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2]$ (M = Rh, **2**; Ir, **3**), in which the organometallic unit "*cis*-$Pt(C{\equiv}CR)_2$" is unusually stabilized by η^2-bis(alkyne) interactions, as has also been confirmed for the related binuclear complex $[(PPh_3)Cp^*Rh(\mu\text{-}1\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Pt(C{\equiv}CSiMe_3)_2]$, **4b**, which has been prepared analogously. These binuclear tetraalkynyl complexes can be used as precursors to unusual bis(double-alkynide)-bridged trinuclear derivatives $[(PEt_3)Cp^*M(\mu\text{-}1\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CR)_2Pt(\mu\text{-}2\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (M = Rh, **5**; Ir, **6**) by displacement reactions of thf from $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$. An X-ray diffraction study confirms that in complex **5b** ($R = SiMe_3$) the mononuclear rhodium fragment "$Cp^*Rh(C{\equiv}CSiMe_3)_2(PEt_3)$" acts as a chelating bidentate ligand toward the alkynyl-bridged diplatinum organometallic unit $Pt(\mu\text{-}1\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CSiMe)_2\text{-}Pt(C_6F_5)_2$.

Introduction

The literature is now rich in studies involving the preparation and chemistry of alkynyl-bridged binuclear complexes $L_nM(\mu\text{-}C{\equiv}CR)_2M'L_n'$,[1] which are attractive due to their structural aspects and reactivity. Surprisingly enough, only a few examples of trinuclear complexes with the metal centers doubly bridged by alkynyl ligands have been reported.[2,3] In these molecules the central metal core $[M](1\kappa C^\alpha\text{-}C{\equiv}CR)_4$ ([M] = M or ML_n) can usually be regarded as a simple bis-chelating ligand bridging two identical neutral or cationic fragments (**A**, Chart 1).[2c−e,3a−f] Three examples of trinuclear cations M_2M' (Pt_2Ag,[3f] Ti_2Ag,[2f] Pt_2Cu[2b]) formed by two orthogonal "$L_nM(C{\equiv}CR)_2$" fragments acting as bidentate diyne ligands toward Cu(I) or Ag(I) (**B**, Chart 1), and a trimetallic mixed valence complex $[Yb_3Cp^*_4(C{\equiv}CPh)_4]$,

Chart 1



A) [M] = Pt; $M'L_n$ = $CuBr_2$, $CoCl_2$, $HgCl_2$. [M] = Zn, V(tmen); $M'L_n$ = Li(tmen). **B**) ML_n = Pt(dppe); M' = Cu. ML_n = *cis*-$Pt(PPh_3)_2$, $Ti(C_5H_4SiMe_3)_2$; M' = Ag. **C**) [Yb] = $Yb(C_5Me_5)_2$. **D**) [Pt] = $Pt(C_6F_5)_2$

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(1) See for example: (a) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113. (b) Pavankumar, P. N. V.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125, and references therein. (c) Ara, I.; Fernández, S.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5923. (d) Zhang, D.; McConville, D. B.; Harbusa, J. M.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 3506. (e) Schottek, J.; Erker, G.; Fröchlich, R. *Eur. J. Inorg. Chem.* **1998**, 551. (f) Mihan, S.; Weidmann, T.; Weinrich, V.; Fenske, D.; Beck, W. *J. Organomet. Chem.* **1997**, *541*, 423. (g) Yam, V. W.-W.; Lee, W.-K.; Cheung, K. K.; Lee, H.-K.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1996**, 2889. (h) Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Rennie, M. A.; Russell, C. A.; Wright, D. S. *Organometallics* **1994**, *13*, 4967. (i) Olbrich, F.; Behrems, U.; Weiss, E. *J. Organomet. Chem.* **1994**, *472*, 365. (j) Cuenca, T. M.; Gómez, R.; Gómez-Sal, P.; Rodrígez, G. M.; Royo, P. *Organometallics* **1992**, *11*, 1229. (k) Varga, V.; Mach, K.; Hiller, J.; Thewalt, U.; Sedmera, P.; Polásek, M. *Organometallics* **1995**, *14*, 1410. (l) Rosenthal, U.; Pulst, S.; Arndt, P.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. *Organometallics* **1995**, *14*, 2961, and references therein.

(2) (a) Boncella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710. (b) Yamazaki, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3051. (c) Edwards, A. J.; Fallaize, A.; Raithby, P. R.; Rennie, M. A.; Steiner, A.; Verhovevoort, K. L.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1996**, 133. (d) Kawaguchi, H.; Tatsumi, K. *Organometallics* **1995**, *14*, 4294. (e) Zhang, D.; McConville, D. B.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1997**, *16*, 824. (f) Hayashi, Y.; Osawa, M.; Kobayashi, K.; Sato, T.; Sato, M.; Wakatsuki, Y. *J. Organomet. Chem.* **1998**, *569*, 169.

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containing symmetrically bridging σ-C≡CPh ligands (**C**, Chart 1),[2a] have also been reported. The use of [Pt(C≡CR)$_4$]$^{2-}$ moieties (**1**, R = *t*-Bu **a**, SiMe$_3$ **b**, Ph **c**) as precursors to homo- and heteroalkynyl-bridged platinum complexes has allowed us to isolate a variety of bi- and trinuclear species, in which the alkynyl entities of the tetraalkynyl platinate precursor remain σ-bonded to the platinum center and coordinate to the metal atom of one [Pd(C$_3$H$_5$)][3d] or two [HgX$_2$,[3a] CoCl$_2$,[3b] AgL,[3c] Pd(C$_3$H$_5$),[3d] Rh(COD),[3e] MX (M = Ag, Cu; X = Cl, Br)[3c]] units in an η^2 fashion. Surprisingly, in similar reactions with 2 equiv of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$], the alkynylplatinates act as monoalkynylating agents toward one of the two "*cis*-Pt(C$_6$F$_5$)$_2$" units, yielding trimetallic compounds possessing both a chelating *cis*-platinate and a σ/π doubly alkynyl bridged system[4] (**D**, Chart 1).

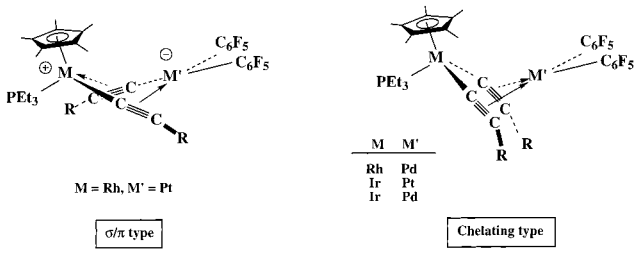
In this paper we report on the use of the anions [Pt(C≡CR)$_4$]$^{2-}$ (R = *t*-Bu, SiMe$_3$, Ph) as double alkynylation reagents. The efficiency of this behavior is demonstrated in the synthesis of a series of heterobimetallic chelating bis(alkyne) derivatives [(PEt$_3$)Cp*M(μ-C≡CR)$_2$Pt(C≡CR)$_2$] (M = Rh, **2**; Ir, **3**), formed via migration of two σ-alkynyl groups from Pt to Rh or Ir. These complexes are the first in which bis(alkynyl)platinum substrates are stabilized by η^2-alkyne interactions. The use of these binuclear derivatives (**2**, **3**) as precursors to a series of unusual asymmetric trinuclear double bis(alkynyl) compounds [(PEt$_3$)Cp*M(μ-C≡CR)$_2$-Pt(μ-C≡CR)$_2$Pt(C$_6$F$_5$)$_2$] (M = Rh, **5a**,**b**; Ir, **6a**−**c**) and the X-ray crystal structure determination of **5b** are also presented in this paper.

Results and Discussion

We have recently found that when the homoleptic platinum substrates **1** react with 2 equiv of Rh(I) solvento species [Rh(COD)S$_2$]$^+$, the platinum centers retain the σ-coordination to the alkynyl fragments, providing neutral 1:2 adducts of the type **A** (Chart 1).[5] Despite the presence of electrophilic Rh centers, no alkynylation processes were observed, indicating that the Pt center has a greater preference for the electron density associated with the sp α-carbon of the alkynyl groups than does Rh(I). Recent studies on binuclear d^6−d^8 complexes [(PEt$_3$)Cp*M(μ-C≡CR)$_2$M′(C$_6$F$_5$)$_2$] (M = Rh, Ir; M′ = Pt, Pd), which exhibit nonplanar structures, have shown that, in these systems, the metal site preference for σ-alkynyl coordination (Ir−Pt/Pd and Rh−Pd, chelating type; Rh−Pt σ/π) follows the order Ir(III) > Pt(II) > Rh(III) > Pd(II) (Chart 2).[6]

As a continuation of these studies, and aiming to isolate bi- and trinuclear compounds, we have studied the reactivity of the homoleptic platinum substrates

Chart 2



[Pt(C≡CR)$_4$]$^{2-}$ (R = *t*-Bu, SiMe$_3$) **1** toward the solvento species [MCp*(PEt$_3$)(acetone)$_2$]$^{2+}$ (M = Rh, Ir) prepared in situ by treating [MCp*X$_2$(PEt$_3$)] (M = Rh, X = Cl; M = Ir, X = I) with AgClO$_4$ (2 equiv) in acetone. All efforts to obtain trinuclear doubly alkynyl bridged M−Pt−M complexes by addition of 0.5 equiv of [Pt(C≡CR)$_4$]$^{2-}$ (R = *t*-Bu **a**, SiMe$_3$ **b**, Ph **c**) to solutions of [MCp*(PEt$_3$)(acetone)$_2$]$^{2+}$ (∼1 equiv) were unsuccessful, even at low temperatures (−30 °C). Probably due to a complex decomposition reaction (characterized by ^{31}P NMR), only compounds **2a** (M = Rh and R = *t*-Bu) and **3c** (M = Ir and R = Ph) were isolated, and in very low yield (∼10% based in Pt), while in the other cases a mixture of compounds, which we were not able to identify, was obtained from the resulting dark solutions. In contrast, the reactions between [Pt(C≡CR)$_4$]$^{2-}$ (R = *t*-Bu **1a**, SiMe$_3$ **1b**, Ph **1c**) and 1 equiv of the dicationic substrate [MCp*(PEt$_3$)(acetone)$_2$]$^{2+}$ at low temperature (−20 °C) (Scheme 1) give the neutral binuclear compounds [(PEt$_3$)Cp*M(μ-C≡CR)$_2$Pt(C≡CR)$_2$] (M = Rh, **2a**,**b**; Ir, **3**), which are isolated in moderate (∼48%, M = Rh) or low (M = Ir, 23% **3a**, 28% **3b**) yields, except complex **3c** (80% yield) (see Experimental Section for details). The analogous phenylethynyl derivative **2c** could not be isolated, presumably due to their extremely low stability in solution, even at low temperatures (−30 °C). The reaction mixture decomposes within seconds. In fact, complexes **2a**,**b** and **3a**−**c** are moderately air-stable as solids, but they also decompose in solution. Unfortunately, we have not been able to obtain suitable crystals for an X-ray analysis of any of these derivatives (**2**, **3**). With the aim of obtaining structural information for one complex of the same nature as **2** or **3**, we prepared the analogous triphenylphosphine derivative **4b**, which was obtained in low yield (25%) starting from **1b** and the corresponding solvento species [RhCp*(PPh$_3$)(acetone)$_2$](ClO$_4$)$_2$ prepared in situ. Because of poor crystal quality, the structure analysis is not of high accuracy. Nevertheless, the connectivity, shown in Scheme 1, was unequivocally established, confirming the presence of a neutral "Cp*(PPh$_3$)Rh(C≡CSiMe$_3$)$_2$" fragment, which acts as a chelating diyne ligand toward the fragment "Pt(σ-C≡CSiMe$_3$)$_2$". For the triethylphosphine derivatives **2** and **3**, their spectroscopic data (similar to those of **4b**) and, indirectly, the molecular structure of **5b** support the chelating formulation drawn in Scheme 1. The mass spectra confirm their binuclear nature, through the observation of peaks whose isotopic distributions correspond to those expected for the binuclear fragments, and also support the double alkynyl migration process through the presence of peaks assignable to the loss of the platinum "Pt(C≡CR)$_2$" fragment, such as [MCp*(PEt$_3$)(C≡C*t*-Bu)$_2$] (*m*/*z* 518, 37%, **2a**; 609, 10%, **3a)** or [MCp*(PEt$_3$)(C≡CR)] (*m*/*z* 527, 100%, **3a**; 453, 26%, **2b**),

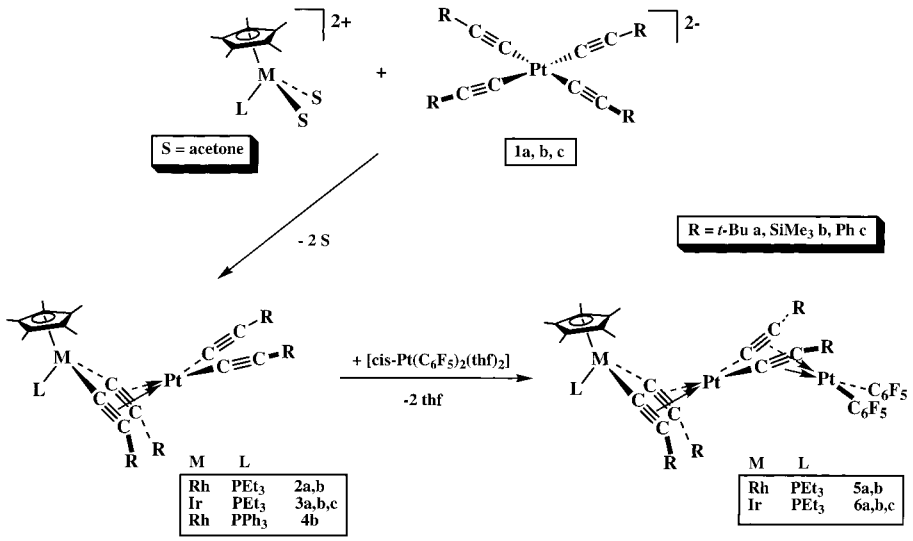
(3) (a) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *J. Chem. Soc., Dalton Trans.* **1994**, 3343. (b) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E. *Inorg. Chim. Acta* **1997**, *264*, 199. (c) Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *J. Organomet. Chem.* **1995**, *490*, 179. (d) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F. *Organometallics* **1996**, *15*, 4537. (e) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E. *Organometallics* **1997**, *16*, 3921. (f) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E.; Moreno, M. T. *J. Organomet. Chem.* **1996**, *510*, 63.

(4) Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *J. Chem. Soc., Dalton Trans.* **1994**, 135.

(5) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E. *Organometallics* **1997**, *16*, 3921.

(6) Ara, I.; Berenguer, J. R.; Eguizábal, E.; Forniés, J.; Lalinde, E.; Martín, A.; Martínez, F. *Organometallics* **1998**, *17*, 4578.

Scheme 1



respectively. The presence of bridging and terminal alkynyl groups in all complexes is inferred from the IR data. The ν(C≡C) absorptions of the bridging ligands (1940−2077 cm^{-1}) and, particularly, the $\Delta\nu$(C≡C)$_{(average)}$ shift relative to the [MCp*(C≡CR)$_2$(PEt$_3$)][6] monomers (36 cm^{-1} for **3c** to 116 cm^{-1} for **2a**) are consistent with a simple complexation of the "Pt(C≡CR)$_2$" unit by the bis(alkynyl) d^6 fragment, both formed via a double intramolecular alkynyl migration from Pt to Rh or Ir. Larger shifts should be expected for a σ/π type double alkynyl bridging system resulting from a simple monoalkynyl migration.[1e,6,7] Moreover, the ν(C≡C) bands due to the terminal alkynyl groups (2015−2127 cm^{-1}) are significantly shifted to higher frequencies in relation to the platinum precursors. As has been previously noted,[4,7a,8] this fact can be interpreted as a consequence of the alkynylation process, which reduces the net charge on the Pt center. Due to the decrease in electron density, the Pt atom is a worse π-back donor toward the remaining C≡CR ligands in the resulting neutral "Pt(C≡CR)$_2$" fragment. Actually, the position of these latter bands is comparable to that observed for bis(alkynyl)platinum fragments stabilized by neutral ligands (e.g., [*cis*-Pt(C≡C*t*-Bu)$_2$L$_2$], L = PPh$_3$ 2123 cm^{-1},[7a] PPh$_2$H 2118 cm^{-1};[9] [*trans*-Pt(C≡CSiMe$_3$)$_2$(PPh$_3$)$_2$], 2041 cm^{-1} [7b]). Although the low stability of **2** and **3** in solution precludes characterization by ^{13}C NMR spectroscopy, the corresponding spectrum of **4b** was simple and displays the alkynyl carbon resonances in the usual range with the expected splitting pattern [bridging C$_\alpha$ 112.03 (dd, $^1J_{C-Rh}$ = 44.8, $^2J_{C-P}$ = 26.9), C$_\beta$ 102.76 (dd, $^2J_{C-Rh}$ = 7.8, $^3J_{C-P}$ = 2.3); terminal C$_\alpha$ 104.26 (d, J = 2.4), C$_\beta$ 101.73(s)]. The proton spectra contain, in addition to signals due to the Cp* and PEt$_3$ ligands, resonances assigned to bridging and terminal C≡CR ligands. In each case, the *t*-Bu and SiMe$_3$ signals which appear at lower frequencies [δ 1.17, **2a**, **3a** (*t*-Bu); 0.06, **2b**; 0.05, **3b**; −0.01, **4b** (SiMe$_3$)] are assigned to terminal groups by comparison with the analogous resonance in **1** (δ 1.14, **1a**; 0.02, **1b**). The more deshielded resonances [δ 1.32, **2a**; 1.34, **3a** (*t*-Bu); and 0.22, **2b**, **3b**; 0.07 **4b** (SiMe$_3$)] are tentatively attributed to bridging alkynyl ligands. Similar spectra (^{1}H and ^{31}P NMR) were observed at low temperature (−50 °C), thus suggesting the presence of only one isomer or a rapid interconversion of conformers in solution. In accord with previous results[6,10] and the structural disposition found for the related triphenylphosphine **4b**, the formation of the conformer with the "Pt(C≡CR)$_2$" fragment endo to the Cp* ligand is suggested (see Scheme 1). This assumption is also consistent with the relative disposition of the central platinum atom in the final trinuclear derivative **5b**.

The formation of **2** and **3** is remarkable for several reasons. First, double alkynylation processes are very rare, and only recently have we reported the first examples observed by reacting the mixed alkynyl substrates [*cis*-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$]$^{2-}$ (R = Ph, SiMe$_3$) with the iridium(III) species [Cp*Ir(PEt$_3$)(acetone)$_2$]$^{+2}$.[6,10] In this context, it is worth noting that a double alkynyl migration has also been suggested recently by Choukroun et al. to explain the formation of the coupled products [Cp$_2$V(μ-η^2:η^4-butadiyne)MCp′$_2$] (Cp′ = Cp, M = Ti, Zr; Cp′ = C$_5$H$_4$SiMe$_3$, M = Zr), starting from [Cp′$_2$M(C≡CPh)$_2$] and vanadocene.[11]

Moreover, we had previously found that replacing Ir with Rh in the above reaction did not yield the analogous rhodium derivatives; rather binuclear σ/π complexes [(PEt$_3$)Cp*Rh(μ-C≡CR)$_2$Pt(C$_6$F$_5$)$_2$] (R = Ph, SiMe$_3$), resulting from a single alkynyl migration from [*cis*-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$]$^{2-}$ to [RhCp*(PEt$_3$)(acetone)$_2$]$^{2+}$, were isolated. These formally zwitterionic complexes are also formed starting from neutral [RhCp*(C≡CR)$_2$(PEt$_3$)] and "Pt(C$_6$F$_5$)$_2$" precursors, showing that the Rh center has, in these species, lesser preference for the σ-coor-

(7) (a) Forniés, J.; Gómez-Saso, M. A.; Lalinde, E.; Martínez, F.; Moreno, M. T. *Organometallics* **1992**, *11*, 2873. (b) Berenguer, J. R.; Forniés, J.; Martínez, F.; Cubero, J.; Lalinde, E.; Moreno, M. T.; Welch, A. J. *Polyhedron* **1993**, *12*, 1797. (c) Erker, G. Frömberg, W.; Bern, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911.

(8) (a) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F.; Urriolabeitia, E.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1291. (b) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F. *Organometallics* **1996**, *14*, 2532.

(9) Falvello, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Sacristán, J. *Chem. Eur. J.* **1999**, *5*, 474.

(10) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1227.

(11) Danjoy, C.; Zhao, J.; Donnadieu, B.; Legros, J.-P.; Valade, L.; Choukron, R.; Zwick, A.; Cassoux, P. *Chem. Eur. J.* **1998**, *4*, 1100.

dination than does platinum(II).[6] So the formation of [(PEt$_3$)Cp*Rh(μ-C≡CR)$_2$Pt(C≡CR)$_2$] (**2**) is surprising and reveals the importance of the electron-withdrawing nature of the C_6F_5 groups in the stabilization of the σ/π zwitterionic complexes.

Finally, the synthesis of these complexes confirms the special ability of bis(alkynyl) metal building blocks to stabilize unusual organometallic entities, as has been previously noted.[12] As far as we know, these molecules are the first examples in which the neutral "Pt(σ-C≡CR)$_2$" unit is stabilized only by η^2-acetylene fragments as coligands. The most closely related compounds are the mononuclear derivatives [Pt(C≡CR)$_2$(COD)].[7a,13] Moreover, we have previously observed that, while [IrCp*(C≡CR)$_2$(PEt$_3$)] with R = Ph or SiMe$_3$ are easily prepared from [IrCp*X$_2$(PEt$_3$)] using classical metal−halogen exchange reactions, all attempts to prepare the *tert*-butyl analogue (R = *t*-Bu) were unsuccessful.[6] As is shown in Scheme 1, the reaction between [Pt(C≡C*t*-Bu)$_4$]$^{2-}$ and [IrCp*(PEt$_3$)(acetone)$_2$]$^{+2}$ provides the elusive "IrCp*(C≡C*t*-Bu)$_2$(PEt$_3$)" unit, which seems to be stabilized in the final dimer **3a**.

This motion is confirmed by the utility of the binuclear products as starting materials for higher nuclearity compounds. The rather more stable bis(double-alkynide)-bridged unsymmetrical trinuclear complexes [(PEt$_3$)Cp*M(μ-C≡CR)$_2$Pt(μ-C≡CR)$_2$Pt(C$_6$F$_5$)$_2$] (M = Rh, **5a**,**b**; Ir, **6**) are easily obtained in moderate yields (≈45−66%) when the organometallic bis(alkyne) "ligands" **2** and **3** are reacted with equimolar amounts of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$]. The ^{1}H and ^{31}P NMR data of **5** and **6** are similar to those of the binuclear precursors, confirming the presence of two inequivalent sets of alkynyl ligands (^{1}H NMR, see Experimental Section). However, their IR spectra only exhibit ν(C≡C) absorptions in the range expected for carbon−carbon triple bonds coordinated to transition metal centers. The ^{19}F NMR spectra of *tert*-butyl and trimethylsilyl derivatives **5a**,**b** and **6a**,**b** confirm the presence of "*cis*-Pt(C$_6$F$_5$)$_2$" fragments with nonrotating C$_6$F$_5$ groups; a set of five signals (AFMRX system) reveals the presence of a symmetry plane containing the three metal centers. Similar spectra were observed at low temperature, discounting the possibility of different conformers in solution. Upon increasing the temperature (up to 40−45 °C) the usual broadening of the *o*-F and *m*-F signals takes place, but coalescence of the two *o*-F and two *m*-F resonances is not reached. By contrast, the phenyl derivative **6c**, as has been previously observed for related systems,[6] seems to be less rigid in solution. Thus, a similar pattern is observed only at low temperature. Upon heating, the two halves of each C$_6$F$_5$ ring average, giving rise to an AA′MXX′ system, probably due to a fast motion of the Pt(C$_6$F$_5$)$_2$ unit above and below of the central platinum coordination plane (see Experimental Section).

The structure of complex **5b** has been established by an X-ray diffraction study (Figure 1). The most interesting, as well as unprecedented, feature of this alkynyl-bridged trinuclear complex is that in both chelating systems the dative bonds point in the same direction (Scheme 1: **5** or **6**) in contrast to the usual arrangement (Chart 1: **A** or **B**), which is topologically centric. As expected, the η^2-coordination of both C≡CSiMe$_3$ triple bonds to the neutral platinum atom Pt(1) reduces the bite angle C(1)−Rh−C(6) to 76.9(5)° (Table 1). This angle is similar to those observed in related Ir−Pt,Pd dimers [(PEt$_3$)Cp*Ir(μ-η^2-C≡CR)$_2$M(C$_6$F$_5$)$_2$] [M/R Pt/Ph 79.9(8)°, Pt/SiMe$_3$ 81.0(7)°, Pd/Ph 81.0(7)°][6] and similar as well to the analogous bite angle at Pt(1) [C(27)−Pt(1)−C(32) 78.2(5)°]. Although both platinum atoms have square-planar geometries, their coordination environments are different. The stabilization of the platinum organometallic moiety "*cis*-Pt(C$_6$F$_5$)$_2$" by acetylenic fragments such as PhC≡CPh[14] or L$_n$M(C≡CR)$_2$[1c,6,7a,10] is now well established. In this complex the terminal "Pt(2)(C$_6$F$_5$)$_2$" unit is symmetrically η^2-bonded to the alkynyl fragments of the binuclear entity "(PEt$_3$)Cp*Rh(μ-C≡CSiMe$_3$)$_2$Pt(C≡CSiMe$_3$)$_2$", with Pt(2)−C(acetylenic) distances [2.303(14)−2.364(15) Å] similar to those found for related derivatives.[1c,6,7a] The central platinum atom Pt(1) is σ-bonded to two C$_\alpha$ atoms of two alkynyl bridging ligands and completes its environment by η^2-coordination of the two alkyne groups of the organometallic entity "RhCp*(C≡CSiMe$_3$)$_2$(PEt$_3$)". Despite the interaction of C(27) and C(32) with Pt(2), the σ Pt(1)−C(27,32) bond distances are quite short [1.94(2), 1.93(2) Å], perhaps reflecting the low trans influence of the η^2-alkyne fragments.[7b] Significantly, the platinum to carbon distances within the bis(η^2-alkyne)−Pt(1) entity [2.282(14)−2.39(2) Å] fall into essentially the same range as the values found in the other chelating bis(alkyne) entity, and accordingly, the deviations of all M−C≡C−SiMe$_3$ (M = Rh, Pt) skeletons from linearity are rather similar and within the usual range found for related chelating type (V-shape) {L$_n$M(C≡CR)$_2$}M′L′$_n$ systems.[1c,3a,6,7a,10]

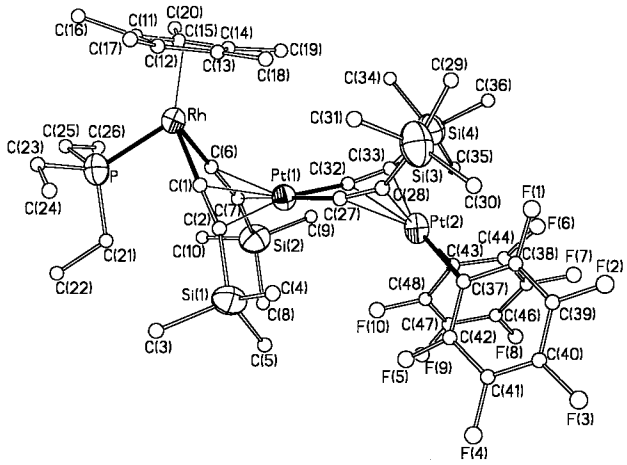


Figure 1. View of the molecular structure of complex **5b**, showing the atom-numbering scheme. Hydrogen atoms have been omitted for clarity.

The Pt centers are located out of the best least-squares plane through the corresponding 3-metalla-1,4-diyne M(C≡C)$_2$ entities (Pt(1), 0.0955 Å; Pt(2), 0.0762 Å). The molecule as a whole has a pseudo-trans arrange-

(12) (a) Janssen, M. D.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817. (b) Kovács, A.; Frenking, G. *Organometallics* **1999**, *18*, 887.

(13) (a) Falvello, L. R.; Fernández, S.; Forniés, J.; Lalinde, E.; Martínez, F.; Moreno, M. T. *Organometallics* **1997**, *16*, 1326. (b) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987.

(14) Usón, R.; Forniés, J.; Tomás, M.; Menjón, B.; Fortuño, C.; Welch, A. J.; Smith, D. E. *J. Chem. Soc., Dalton Trans.* **1993**, 275.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 5b

Pt(1)−C(32)	1.93(2)	Pt(1)−C(27)	1.94(2)	Pt(1)−C(2)	2.282(14)
Pt(1)−C(1)	2.322(14)	Pt(1)−C(7)	2.341(14)	Pt(1)−C(6)	2.39(2)
Pt(2)−C(43)	2.029(14)	Pt(2)−C(37)	2.03(2)	Pt(2)−C(33)	2.303(14)
Pt(2)−C(28)	2.331(15)	Pt(2)−C(32)	2.34(2)	Pt(2)−C(27)	2.364(15)
Rh−C(6)	1.96(2)	Rh−C(1)	2.017(15)	Rh−C(15)	2.19(2)
Rh−C(12)	2.208(13)	Rh−C(13)	2.239(14)	Rh−C(11)	2.24(2)
Rh−C(14)	2.246(14)	Rh−P	2.287(3)	Rh−*Cent	1.878
C(1)−C(2)	1.19(2)	C(6)−C(7)	1.25(2)	C(27)−C(28)	1.24(2)
C(32)−C(33)	1.24(2)	Rh···Pt(1)	3.297(1)	Pt(1)···(2)	3.366(1)

C(32)−Pt(1)−C(27)	78.2(5)	C(27)−Pt(1)−C(2)	88.5(5)
C(27)−Pt(1)−C(1)	104.3(5)	C(32)−Pt(1)−C(7)	89.8(6)
C(32)−Pt(1)−C(6)	108.5(6)	C(32)−Pt(1)−C(2)	164.5(6)
C(32)−Pt(1)−C(1)	162.5(6)	C(27)−Pt(1)−C(7)	167.4(6)
C(27)−Pt(1)−C(6)	158.7(6)	C(43)−Pt(2)−C(37)	84.0(6)
C(43)−Pt(2)−C(33)	85.2(5)	C(37)−Pt(2)−C(28)	87.3(5)
C(43)−Pt(2)−C(32)	102.3(5)	C(37)−Pt(2)−C(27)	106.9(5)
C(37)−Pt(2)−C(33)	163.9(5)	C(43)−Pt(2)−C(28)	170.9(5)
C(37)−Pt(2)−C(32)	164.9(5)	C(43)−Pt(2)−C(27)	156.6(6)
C(6)−Rh−C(1)	76.9(5)	C(6)−Rh−P	88.2(4)
C(1)−Rh−P	88.7(4)	*Cent−Rh−P	130.8
*Cent[a]−Rh−C(1)	127.8	*Cent−Rh−C(6)	127.4
C(2)−C(1)−Rh	168.4(12)	C(1)−C(2)−Si(1)	163.5(12)
C(7)−C(6)−Rh	170.0(13)	C(6)−C(7)−Si(2)	159.1(13)
C(28)−C(27)−Pt(1)	165.4(13)	C(27)−C(28)−Si(3)	147.7(13)
C(33)−C(32)−Pt(1)	167.1(14)	C(32)−C(33)−Si(4)	156.6(14)

[a] *Cent = centroid of Cp*.

ment of terminal Rh and Pt(2) atoms with respect to the local Pt(1) coordination plane. The diplatinum "Pt(1)(μ-C≡CSiMe$_3$)$_2$Pt(2)(C$_6$F$_5$)$_2$" fragment is oriented endo to the Cp* ring, and the dihedral angle between the fragment "RhC(1)C(6)" and the central Pt(1) coordination plane (62.2°) is significantly greater than the corresponding one between the local Pt(1) and Pt(2) coordination planes (45.3°). The puckering of both bimetallacyclic M(C≡C)$_2$Pt (M = Rh, Pt) cores does not seem to cause any bonding interaction between the metal centers [Rh···Pt(1) 3.297(1) Å, Pt(1)···Pt(2) 3.336(1) Å].

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere. Solvents (hexane, alkane mixture) were dried by standard procedures and distilled under dry N$_2$ before use, and acetone was treated with KMnO$_4$ and distilled under dry N$_2$ prior to use. [NBu$_4$]$_2$[Pt(C≡CR)$_4$]·nH$_2$O **1** (n = 2, R = t-Bu,[15] SiMe$_3$;[4] n = 0, R = Ph[15]), [MCp*X$_2$(PEt$_3$)] (M = Rh, X = Cl; M = Ir, X = I),[6] [RhCp*Cl$_2$(PPh$_3$)],[16] and AgClO$_4$[17] were prepared by published methods.

NMR spectra were recorded on a Bruker ARX-300 spectrometer (all coupling constants are given in Hz). IR spectra were obtained on Perkin-Elmer 883 or Perkin-Elmer FT-IR Spectrum 1000 spectrometers using Nujol mulls between polyethylene sheets. Elemental analyses were carried out with Perkin-Elmer 2400 CHNS/O or Carlo Erba EA1110 CHNS-O microanalyzers. Mass spectra were recorded on a VG Autospec double-focusing mass spectrometer operating in the FAB mode or an HP-5989B mass spectrometer using the ES technique. Mass spectra of complexes **6a**,**b** were obtained using the ES-(+) technique and AgNO$_3$ as ionizing agent.

Safety Note. Perchlorate salts are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparation of [(PEt$_3$)Cp*M(μ-1κC^{α}:η^2-C≡Ct-Bu)$_2$Pt(C≡Ct-Bu)$_2$] (M = Rh, 2a; Ir, 3a). 2a. A solution of [RhCp*Cl$_2$(PEt$_3$)] (0.15 g, 0.35 mmol) in acetone (20 mL) was treated with AgClO$_4$ (0.15 g, 0.70 mmol), and the mixture was stirred at room temperature for 1 h. The AgCl was filtered off, and the filtrate was cooled at −20 °C and treated with [NBu$_4$]$_2$[Pt(C≡Ct-Bu)$_4$]·2H$_2$O (**1a**) (0.35 g, 0.32 mmol). The resulting greenish solution was stirred for 2 min and evaporated to ca. 5 mL, causing the precipitation of **2a** as a yellow solid. Yield: 48.5%. Anal. Calcd for C$_{40}$H$_{66}$PPtRh: C, 54.85; H, 7.59. Found: C, 54.61; H, 7.81. MS(ES−): m/z 876 [M + 1]$^-$ 42; 795 [M − C$_2$$t$-Bu + 1]$^-$ 51; 758 [M − PEt$_3$ + 1]$^-$ 63; 740 [M − Cp* + 1]$^-$ 17; 715 [M − 2C$_2$$t$-Bu − 2]$^-$ 14; 675 [M − PEt$_3$ − C$_2$$t$-Bu − 1]$^-$ 100; 621 [M − Cp* − PEt$_3$]$^-$ 13; 518 [RhCp*(C$_2$$t$-Bu)$_2$(PEt$_3$)]$^-$ 37. IR (cm^{-1}): ν(C≡C) 2127(s), 2081(w), 1994(m). ^{1}H NMR (CDCl$_3$, δ): at 16 °C, 1.93 (d, $^4J_{P-H}$ = 2.8, Cp*, 15H); 1.81 (m, P−CH_2−CH$_3$, 6H); 1.32 (s, t-Bu, 18H); 1.17 (s, t-Bu, 18H); 1.05 (m, P−CH$_2$−CH_3, 9H). ^{31}P NMR (CDCl$_3$, δ): at 16 °C, 41.23 (d, $^1J_{Rh-P}$ = 135.4). The same patterns for the ^{1}H and ^{31}P NMR were observed at −50 °C.

3a. Complex **3a** was prepared, as a beige solid, in a similar way to that for **2a**, starting from 0.16 g (0.23 mmol) of [IrCp*I$_2$(PEt$_3$)], 0.095 g (0.46 mmol) of AgClO$_4$ (2 h of stirring for the formation of [IrCp*(PEt$_3$)(acetone)$_2$](ClO$_4$)$_2$), and 0.24 g (0.23 mmol) of **1a**. Yield: 23%. Anal. Calcd for C$_{40}$H$_{66}$IrPPt: C, 49.77; H, 6.89. Found: C, 49.39; H, 7.18. MS(ES−): m/z 966 [M + 1]$^-$ 7; 883 [M − C$_2$$t$-Bu − 1]$^-$ 7; 846 [M − PEt$_3$ - 1]$^-$ 11; 803 [M − 2C$_2$$t$-Bu − 1]$^-$ 18; 722 [M − 3C$_2$$t$-Bu]$^-$ 60; 609 [IrCp*(C$_2$$t$-Bu)$_2$(PEt$_3$) + 2]$^-$ 10; 527 [IrCp*(C$_2$$t$-Bu)(PEt$_3$) + 1]$^-$ 100; 445 [IrCp*(PEt$_3$) − 2]$^-$ 11%. IR (cm^{-1}): ν(C≡C) 2126(m), 1998(w). ^{1}H NMR (CDCl$_3$, δ): at 16 °C, 2.03 (s br, Cp*, 15H); 1.83 (m, P−CH_2−CH$_3$, 6H); 1.34 (s, t-Bu, 18H); 1.17 (s, t-Bu, 18H); 1.00 (m, P−CH$_2$−CH_3, 9H). ^{31}P NMR (CDCl$_3$, δ): at 16 °C, −0.03 (s). The same patterns for the ^{1}H and ^{31}P NMR were observed at −50 °C.

Preparation of [(PEt$_3$)Cp*M(μ-1κC^{α}:η^2-C≡CSiMe$_3$)$_2$Pt(C≡CSiMe$_3$)$_2$] (M = Rh, 2b; Ir, 3b). 2b. [NBu$_4$]$_2$[Pt(C≡CSiMe$_3$)$_4$]·2H$_2$O (**1b**) (0.34 g, 0.31 mmol) was added to a filtered solution of [RhCp*(PEt$_3$)(acetone)$_2$](ClO$_4$)$_2$ (0.32 mmol) in 5 mL of acetone at −20 °C, prepared from 0.135 g (0.316 mmol) of [RhCp*Cl$_2$(PEt$_3$)] and 0.13 g (0.63 mmol) of AgClO$_4$. Immediately, the resulting brown suspension was evaporated to dryness, and the residue was treated with 30 mL of toluene and filtered. Evaporation of the filtrate to dryness and treat-

(15) Espinet, P.; Forniés, J.; Martínez, F.; Tomás, M.; Lalinde, E.; Moreno, M. T.; Ruiz, A.; Welch A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 791.
(16) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.
(17) Smith, G. F.; Ring, F. *J. Am. Chem. Soc.* **1937**, *59*, 1889.

ment of the residue with cold Et_2O (≈5 mL) yielded complex **2b** as a pale brown solid. Yield: 48.5%. Anal. Calcd for $C_{36}H_{66}PPtRhSi_4$: C, 45.98; H, 7.07. Found: C, 45.75; H, 6.82. MS(FAB+): *m/z* 939 $[M]^+$ 10; 745 $[(PEt_3)Cp^*Rh(C_2SiMe_3)_2Pt]^+$ 26; 648 $[(PEt_3)Cp^*Rh(C_2SiMe_3)Pt]^+$ 57; 453 $[RhCp^*(C_2SiMe_3)(PEt_3)]^+$ 26; 356 $[RhCp^*(PEt_3)]^+$ 94. IR (cm^{-1}): ν(C≡C) 2056(vs), 2037(vs), 1951(vs), 1943(vs). ^1H NMR ($CDCl_3$, δ): at 16 °C, 1.95 (s br, Cp* 15H); 1.81 (m, P−CH_2−CH_3, 6H); 1.05 (m, P−CH_2−CH_3, 9H); 0.22 (s, $SiMe_3$, 18H); 0.06 (s, $SiMe_3$, 18H). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, 40.18 (d, $^1J_{Rh-P}$ = 131.3). The same patterns were observed for the ^1H and ^{31}P NMR at −50 °C.

3b. Complex **3b** was prepared, as a beige solid, by following the synthesis described for **2b**, but starting from 0.20 g (0.29 mmol) of $[IrCp^*I_2(PEt_3)]$, 0.12 g (0.57 mmol) of $AgClO_4$, and 0.30 g (0.27 mmol) of **1b** and treating the final residue with cold hexane (≈5 mL). Yield: 28%. Anal. Calcd for $C_{36}H_{66}IrPPtSi_4$: C, 42.00; H, 6.46. Found: C, 42.19; H, 6.46. MS(ES+): *m/z* 1029 $[M]^+$ 11; 957 $[M - SiMe_3 + 1]^+$ 100. IR (cm^{-1}): ν(C≡C) 2054(vs), 2036(vs), 1954(vs), 1940(vs). ^1H NMR ($CDCl_3$, δ): at 16 °C, 2.05 (d, $^4J_{P-H}$ =1.7, Cp*, 15H); 1.84 (m, P−CH_2−CH_3, 6H); 1.00 (m, P−CH_2−CH_3, 9H); 0.22 (s, $SiMe_3$, 18H); 0.05 (s, $SiMe_3$, 18H). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, −0.96 (s).

Preparation of [(PEt$_3$)Cp*Ir(μ-1κC^α:η^2-C≡CPh)$_2$Pt(C≡CPh)$_2$], 3c. The addition of $[NBu_4]_2[Pt(C≡CPh)_4]$ (**1c**) (0.18 g, 0.17 mmol) to a filtered solution of $[IrCp^*(PEt_3)(acetone)_2](ClO_4)_2$ (0.17 mmol) in 5 mL of acetone at −20 °C, prepared from 0.12 g (0.17 mmol) of $[IrCp^*Cl_2(PEt_3)]$ and 0.07 g (0.34 mmol) of $AgClO_4$, caused the immediate precipitation of complex **3c** as a beige solid, which was filtered and washed with cold acetone (≈5 mL). Yield: 84%. Anal. Calcd for $C_{48}H_{50}PPtIr$: C, 55.16; H, 4.82. Found: C, 55.14; H, 4.91. MS(ES+): *m/z* 1046 $[M + 1]^+$ 3. IR (cm^{-1}): ν(C≡C) 2108 (m), 2077(vs). ^1H NMR ($CDCl_3$, δ): at 16 °C, 7.83, 7.22, 6.96 (m, Ph, 20H); 2.20 (d, $^4J_{P-H}$ =1.5, Cp*, 15H); 1.82 (m, P−CH_2−CH_3, 6H); 1.03 (m, P−CH_2−CH_3, 9H). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, 1.98 (s). The same patterns were observed for the ^1H and ^{31}P NMR at −50 °C.

Preparation of [(PPh$_3$)Cp*Rh(μ-1κC^α:η^2-C≡CSiMe$_3$)$_2$Pt(C≡CSiMe$_3$)$_2$], 4b. A filtered solution of $[RhCp^*(PPh_3)(acetone)_2](ClO_4)_2$ (0.30 mmol) in 10 mL of acetone at −20 °C [prepared from 0.17 g (0.30 mmol) of $[RhCp^*Cl_2(PPh_3)]$ and 0.12 g (0.30 mmol) of $AgClO_4$ with 1 h of stirring] was treated with 0.31 g (0.27 mmol) of **1b**. Immediately, the resulting brown solution was evaporated to dryness and the residue treated with cold EtOH (≈5 mL), yielding complex **4b** as a yellow solid. Yield: 25%. Anal. Calcd for $C_{48}H_{66}PPtRhSi_4$: C, 53.17; H, 6.13. Found: C, 53.35; H, 6.56. MS(ES+): *m/z* 1084 $[M + 1]^+$ 19; 1013 $[M - SiMe_3 + 2]^+$ 88; 985 $[M - C_2SiMe_3 - 2]^+$ 17; 890 $[M - 2C_2SiMe_3]^+$ 42; 822 $[M - PPh_3]^+$ 29; 597 $[RhCp^*(C_2SiMe_3)(PPh_3)]^+$ 20; 499 $[RhCp^*(PPh_3) - 1]^+$ 17. IR (cm^{-1}): ν(C≡C) 2063(vs), 2044(vs), 1955(s), 1948(s). ^1H NMR ($CDCl_3$, δ): at 16 °C, 7.56, 7.36 (m, PPh_3, 15H); 1.63 (d, $^4J_{P-H}$ = 3.4, Cp*, 15H); 0.08 (s, $SiMe_3$, 18H); −0.02 (s, $SiMe_3$, 18H). ^{13}C NMR ($CDCl_3$, δ): at 16 °C, 134.07 (d, $^2J_{C-P}$ = 10.4, *o*-C, PPh_3); 130.21 (d, $^4J_{C-P}$ = 1.9, *p*-C, PPh_3; this signal overlaps with one of the signals of the doublet due to the *i*-C (PPh_3), which is centered at δ ∼130); 127.83 (d, $^3J_{C-P}$ = 10.4, *m*-C, PPh_3); 112.03 (dd, $^1J_{C-Rh}$ = 44.8, $^2J_{C-P}$ = 26.9, C_α, RhC≡CSiMe$_3$); 104.26 (d, *J* = 2.4, C_α, PtC≡CSiMe$_3$); 103.50 (dd, $^1J_{C-Rh}$ = 4.2, $^2J_{C-P}$ = 2.5, C_5Me_5); 102.76 (dd, $^2J_{C-Rh}$ = 7.8, $^3J_{C-P}$ = 2.3, C_β, RhC≡CSiMe$_3$); 101.73 (s, C_β, PtC≡CSiMe$_3$); 9.47 (dd, $^2J_{C-Rh}$ = 2.3, $^3J_{C-P}$ = 1.6, $C_5(CH_3)_5$); 1.11 (s, $SiMe_3$); 0.94 (s, $SiMe_3$). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, 41.91 (d, $^1J_{Rh-P}$ = 138.6). The same patterns for the ^1H, ^{13}C, and ^{31}P NMR were observed at −50 °C.

Preparation of [(PEt$_3$)Cp*M(μ-1κC^α:η^2-C≡CR)$_2$Pt(μ-2κC^α:η^2-C≡CR)$_2$Pt(C$_6$F$_5$)$_2$] (M = Rh; R = *t*-Bu 5a, SiMe$_3$ 5b; M = Ir; R = *t*-Bu 6a, SiMe$_3$ 6b, R = Ph 6c). 5a. To a cooled (−20 °C) solution of **2a** (0.092 g, 0.11 mmol) in CH_2Cl_2 (10 mL) was added $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$ (0.071 g, 0.11 mmol). The resulting garnet solution was stirred for 5 min and evaporated to dryness. Treatment of the residue with cold Et_2O (≈5 mL) afforded complex **5a** as a yellow solid. Yield: 64.4%. Anal. Calcd for $C_{52}F_{10}H_{66}PPt_2Rh$: C, 44.45; H, 4.73. Found: C, 44.41; H, 4.95. MS(FAB+): *m/z* 1404 $[M]^+$ 2; 758 [**2a** − PEt_3 + 1]$^+$ 61; 677 [**2a** − PEt_3 − C_2t-Bu + 1]$^+$ 11; 437 $[RhCp^*(C_2t\text{-}Bu)(PEt_3)]^+$ 25; 356 $[RhCp^*(PEt_3)]^+$ 59. IR (cm^{-1}): ν(C≡C) 1997(s); $\nu(C_6F_5)_{x-sensitive}$ 799(vs), 786(vs). ^1H NMR ($CDCl_3$, δ): at 16 °C, 1.95 (d, $^4J_{P-H}$ = 2.6 Hz, Cp*, 15H); 1.87 (m, P−CH_2−CH_3, 6H); 1.32 (s, *t*-Bu, 18H); 1.11 (m, P−CH_2−CH_3, 9H); 1.08 (s, *t*-Bu, 18H). ^{19}F NMR ($CDCl_3$, δ): at 16 °C, −113.31 (dm, 2 *o*-F), −114.04 (m, 2 *o*-F) (^{195}Pt satellites are barely observed due to its low solubility); −164.81 (t, 2 *p*-F); −165.85 (m, 2 *m*-F); −166.20 (m, 2 *m*-F). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, 39.79 (d, $^1J_{Rh-P}$ = 130.8). Similar spectra were observed for the ^1H, ^{19}F, and ^{31}P NMR at −50 °C.

5b. Complex **5b** was prepared as a yellow solid using a method similar to that described for **5a** and starting from 0.12 g (0.13 mmol) of **2b** and 0.086 g (0.13 mmol) of *cis*-$[Pt(C_6F_5)_2(thf)_2]$. Yield: 54.5%. Anal. Calcd for $C_{48}F_{10}H_{66}PPt_2RhSi_4$: C, 39.24; H, 4.43. Found: C, 38.93; H, 4.49. MS(ES−): *m/z* 1351 $[M - PEt_3 + 1]^-$ 80; 1334 $[M - Cp^* + 1]^-$ 52; 1227 $[M - PEt_3 - SiMe_3]^-$ 35; 1183 $[M - PEt_3 - C_6F_5]^-$ 14; 1143 $[M - Cp^* - SiMe_3 - PEt_3 + 1]^-$ 52; 973 $[M - Cp^* - C_6F_5 - SiMe_3 - PEt_3 - 2]^-$ 28. IR (cm^{-1}): ν(C≡C) 1952(vs), 1937(vs), 1928(vs); $\nu(C_6F_5)_{x-sensitive}$ 802(vs), 792(s). ^1H NMR ($CDCl_3$, δ): at 16 °C, 1.95 (d, $^4J_{P-H}$ = 2.7, Cp*, 15H); 1.85 (m, P−CH_2−CH_3, 6H); 1.10 (m, P−CH_2−CH_3, 9H); 0.21 (s, $SiMe_3$, 18H); −0.02 (s, $SiMe_3$, 18H). ^{19}F NMR ($CDCl_3$, δ): at 16 °C, −114.11 (m, $^3J_{Pt-o-F}$ = 432, 2 *o*-F); −114.36 (d, $^3J_{Pt-o-F}$ = 445, 2 *o*-F); −165.05 (t, 2 *p*-F); −166.18 (m, 2 *m*-F); −166.63 (m, 2 *m*-F). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, 40.16 (d, $^1J_{Rh-P}$ = 129.4). Similar spectra were observed for the ^1H, ^{19}F, and ^{31}P NMR at low temperature (−50 °C). In the ^{19}F NMR spectra, although only a broad signal is observed at 45 °C for both the *o*-F and the *m*-F, the T_c has still not been reached.

6. Complexes **6** were prepared as white (**6a**), beige (**6b**), or brown (**6c**) solids in a way similar to that described for **5a**, but treating the final residue with cold EtOH (≈5 mL). [**6a**: 0.11 g (0.11 mmol) of **3a** and 0.077 g (0.11 mmol) of $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$. Yield: 51%. **6b**: 0.044 g (0.043 mmol) of **3b** and 0.029 g (0.043 mmol) of $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$. Yield: 45%. **6c**: 0.12 g (0.11 mmol) of **3c** and 0.077 g (0.11 mmol) of $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$. Yield: 66%.]

Data for 6a. Anal. Calcd for $C_{52}F_{10}H_{66}IrPPt_2$: C, 41.79; H, 4.45. Found: C, 41.86; H, 4.58. MS(ES+): *m/z* 1603 [M + Ag + 1]$^+$ 25; 1073 [**3a** + Ag]$^+$ 42; 715 $[IrCp^*(C_2t\text{-}Bu)_2(PEt_3) + Ag]^+$ 100. IR (cm^{-1}): ν(C≡C) 1996(w); $\nu(C_6F_5)_{x-sensitive}$ 798(m), 786-(m). ^1H NMR ($CDCl_3$, δ): at 16 °C, 2.05 (d, $^4J_{P-H}$ = 1.6, Cp*, 15H); 1.89 (m, P−CH_2−CH_3, 6H); 1.33 (s, *t*-Bu, 18H); 1.07 (s br, *t*-Bu and P−CH_2−CH_3, 27H). ^{19}F NMR ($CDCl_3$, δ): at 16 °C, −113.37 (dm, 2 *o*-F), −114.04 (m, 2 *o*-F) (^{195}Pt satellites are barely observed due to low solubility); −164.83 (t, 2 *p*-F); −165.91 (m, 2 *m*-F); −166.60 (m, 2 *m*-F). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, −0.15 (s). Similar spectra were observed for the ^1H, ^{19}F, and ^{31}P NMR at low (−50 °C) and high (40 °C) temperatures.

Data for 6b. Anal. Calcd for $C_{48}F_{10}H_{66}IrPPt_2Si_4$: C, 36.99; H, 4.27. Found: C, 36.89; H, 4.47. MS(ES+): *m/z* 1666 [M + Ag]$^+$ 51; 1139 [**3b** + Ag + 2]$^+$ 100; 957 [**3b** + $SiMe_3$ + 1]$^+$ 29. IR (cm^{-1}): ν(C≡C) 1951(vs), 1927(vs); $\nu(C_6F_5)_{x-sensitive}$ = 802-(vs), 791(s). ^1H NMR ($CDCl_3$, δ): at 16 °C, 2.05 (d, $^4J_{P-H}$ = 1.5, Cp*, 15H); 1.88 (m, P−CH_2−CH_3, 6H); 1.05 (m, P−CH_2−CH_3, 9H), 0.22 (s, $SiMe_3$, 18H); −0.03 (s, $SiMe_3$, 18H). ^{19}F NMR ($CDCl_3$, δ): at 16 °C, −114.13 (m, $^3J_{Pt-o-F}$ ≈ 425, 2 *o*-F); −114.36 (dm, $^3J_{Pt-o-F}$ ≈ 435, 2 *o*-F); −165.11 (t, 2 *p*-F); −166.34 (m, 2 *m*-F); −166.60 (m, 2 *m*-F). ^{31}P NMR ($CDCl_3$, δ): at 16 °C, −0.46 (s). Similar ^1H, ^{19}F, and ^{31}P NMR spectra were observed at low (−50 °C) and high (40 °C) temperatures.

Data for 6c. Anal. Calcd for $C_{60}F_{10}H_{50}IrPPt_2$: C, 45.77; H,

3.20. Found: C, 45.83; H, 3.60. MS(ES−): No molecular peak was observed, *m*/*z* 563 $[Pt(C_2Ph)_2(C_6F_5)]^-$ 100. IR (cm^{-1}): ν(C≡C) 2018(w), 1967(w br); $\nu(C_6F_5)_{x-sensitive}$ = 803(vs br). ^1H NMR ($CDCl_3$, δ): at 16 °C, 7.80, 7.25, 7.07, 6.96, 6.79 (m, Ph, 20 H); 2.17 (s, Cp*, 15H); 1.86 (m, P−CH_2−CH_3, 6H); 1.03 (m, P−CH_2−CH_3, 9H). ^{19}F NMR ($CDCl_3$, δ): at 16 °C, −116.49 (d, $^3J_{Pt-o-F} \approx 373$, 4 *o*-F); −164.89 (t, 2 *p*-F); −166.49 (m, 4 *m*-F). The same pattern is observed at 40 °C, but on cooling the *o*-F signal broadens and splits into two different signals (at −5 °C, δ −116.45, −116.64), from which the lower frequency one continues to broaden at lower temperatures (−50 °C, δ −116.28, ca. −117).^{31}P NMR ($CDCl_3$, δ): at 16 °C, 2.21 (s). Similar spectra were observed for the ^1H and ^{31}P NMR at low (−50 °C) and high (40 °C) temperatures.

X-ray Crystal Structure Determination. Suitable crystals of **5b** were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of the complex at −30 °C.

Crystal data and other details of the structure analysis are presented in Table 2. The selected crystal was glued to a glass fiber. Unit cell constants were determined from 25 accurately centered reflections with 21.9° < 2θ < 31.5°. Data were collected using ω-scans. Three check reflections remeasured after every 3 h showed a decay of ca. 13% of the diffracted intensities over the period of data collection. The space group $Pca2_1$ is established (and *Pbcm* is ruled out) by the fact that Z = 4, together with the absence of inversion or 2-fold rotation symmetry in the molecule, and the orientation of the molecular pseudo-symmetry plane, which is not parallel to any of the faces of the orthorhombic cell. In space group *Pbcm* with Z = 4, the molecule would have to lie on either an inversion center, a 2-fold axis, or a crystallographic mirror. The positions of the heavy atoms were determined from the Patterson map. The remaining atoms were located in successive difference Fourier syntheses. H atoms were added at calculated positions (C−H = 0.96 Å), with isotropic displacement parameters assigned as 1.2 times the equivalent isotropic U's of the corresponding C atoms for CH_2 hydrogens, and 1.5 times for CH_3 hydrogens. A final difference electron density map showed no peaks above 1 e $Å^{-3}$ (max 0.94; largest diff hole −0.91). The refinement was carried out using the program SHELXL-93.[18]

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Table 2. Crystal Data and Structure Refinement for 5b

empirical formula	$C_{48}H_{66}F_{10}PPt_2RhSi_4$
fw	1469.46
unit cell dimens	
a (Å)	27.588(2)
b (Å)	10.4447(9)
c (Å)	20.230(2)
volume ($Å^3$), Z	5829.4(8), 4
wavelength (Å)	0.71073
temperature (K)	293(1)
radiation	graphite-monochromated Mo Kα
cryst syst	orthorhombic
space group	$Pca2_1$
abs coeff (mm^{-1})	5.239
transmission factors	0.968, 0.607
abs corr	Ψ scans
diffractometer	Enraf-Nonius CAD4
2θ range for data collectn (deg)	4−50 (+h, +k, +l)
no. of reflns collected	5241
no. of ind reflns	5241
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2 [b]	1.038
final R indices ($I > 2\sigma(I)$)[a]	$R1 = 0.0356$, $wR2 = 0.0805$
R indices (all data)	$R1 = 0.0598$, $wR2 = 0.0912$
abs structure param	0.005(7)

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

Supporting Information Available: Tables giving positional and thermal parameters, bond distances, and bond angles for **5b**. Basic crystallographic data table for **4b**. View of the molecular structure of complex **5b**, showing full ellipsoids for all the atoms at their 50% probability level. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990753Y

(18) Sheldrick, G. M. *SHELXL-93*, a program for crystal structure refinement; University of Göttingen: Germany, 1993.