Synthesis of Heterobridged (μ-C≡CR)(μ-X) (X = PPh_2, PPh_2O) Platinum−Rhodium or Platinum−Iridium Dimers

Larry R. Falvello, Juan Forniés,* and Antonio Martín

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain

Julio Gómez, Elena Lalinde,* M. Teresa Moreno, and Jorge Sacristán

Departamento de Química, Universidad de La Rioja, 26001 Logroño, Spain

Received January 6, 1999

The synthesis and full characterization of a series of heterobimetallic mixed-bridge alkynyl/phosphido platinum−rhodium and alkynyl/phosphinite platinum−rhodium and platinum−iridium complexes is presented. Treatment of *trans*-[Pt(C_6F_5)(C≡CR)(PPh_2H)$_2$] [**2**; R = *t*-Bu (**a**), Ph (**b**)] [generated through the rupture of the homobridged *trans,sym*-[Pt(μ-κC^{α}:η^2-C≡CR)(C_6F_5)(PPh_2H)]$_2$ (**1**) with PPh_2H] or *cis*-[Pt(C≡CR)$_2$(PPh_2H)$_2$] with rhodium acetylacetonate species [Rh(acac)L_2] (L_2 = COD, 2CO) in acetone produces the corresponding alkynyl/diphenylphosphido-bridged complexes *trans,cis*-[(C_6F_5)(PPh_2H)Pt(μ-κC^{α}:η^2-C≡CR)(μ-PPh_2)RhL_2] (L_2 = COD (**3**), 2CO (**4a**)] and *cis,cis*-[(C≡CR)(PPh_2H)Pt(μ-κC^{α}:η^2-C≡CR)(μ-PPh_2)RhL_2] (L_2 = COD (**5**), 2CO (**6a**)]. The related mixed alkynyl/phosphinite complexes [{(PPh_2O)$_2$H}Pt(μ-κC^{α}:η^2-C≡CR)(μ-κP,κO-PPh_2O)ML_2] [ML_2 = RhCOD (**7**), Rh(CO)$_2$ (**8**), IrCOD (**9**)] can be prepared by reacting [Pt(C≡CR){(PPh_2O)$_2$H}(PPh_2OH)] with [M(acac)L_2] (M = Rh, Ir). The molecular structure of **6a**, determined by X-ray diffraction, shows that the alkynyl ligand is σ-bonded to platinum and η^2-bonded to the rhodium center with a platinum−rhodium distance of 3.142(1) Å. Complex **6a** ($C_{38}H_{39}O_2P_2PtRh$) crystallizes in the triclinic system, space group $P\bar{1}$: a = 11.427(2) Å, b = 12.882(2) Å, c = 14.692(2) Å, α = 99.098(14)°, β = 108.339(12)°, γ = 113.11(2)°, V = 1787.2(4) Å^3, and Z = 2.

Introduction

During the past decade, a large number of studies involving the preparation and chemistry of homo- and heterobinuclear complexes containing alkynyl bridging ligands have been reported.[1] Much attention has been paid to doubly alkynyl bridged (μ-C≡CR)$_2$ complexes[2] because of their implication in C−C alkynide coupling processes,[2e,3] as well as C−C bond cleavage in butadiyne ligands induced by metal centers.[2f,4] Binuclear complexes with a single μ-C≡CR moiety have also been studied, particularly because of their relevance as model species for the well-known acetylene−vinylidene tautomerism process.[1d,5] In contrast, derivatives containing a heterobridged system of the type (μ-C≡CR)(μ-X) are less common,[6] and in particular, a very limited number of mixed-bridge μ-phosphido L_nM(μ-C≡CR)(μ-PR'_2)M′L_n[1b,c,7] or μ-phosphinite L_nM(μ-C≡CR)(μ-PR'_2O)M′L_n[8] binuclear complexes have been reported. The main synthetic method for the preparation of homobimetallic compounds of this type is based on the P−C(alkyne) bond cleavage reactions starting from phosphinoalkyne (PR'_2C≡CR) or alkynylphosphine oxides [PR'_2C≡CR(O)], respectively, and metal carbonyls. The only heterobimetallic complex structurally described to date, [Cp_2Ti(μ-κC^{α}:η^2-C≡CPh)(μ-PPh_2)Ni(PPh_3)],[7f] was unexpectedly produced by treatment of the tweezer-like complex [Cp_2Ti(μ-κC^{α}:η^2-C≡C$SiMe_3$)(μ-κC^{α}:η^2-C≡CPh)Ni(PPh_3)] with PPh_3; in this reaction, one Ph group of PPh_3 is selectively coupled with the C≡C$SiMe_3$ fragment to give

(1) (a) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89. (b) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (c) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (d) Akita, M.; Moro-Oka, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420. (e) Forniés, J.; Lalinde, E. *J. Chem. Soc., Dalton Trans.* **1996**, 2587 and references therein. (f) Beck, V.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (g) Lotz, S.; van Rooyen, P. H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219. (h) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113. For some recent work see: Lang, H.; Köhler, K.; Rheinwald, G.; Zsolnai, L.; Büchner, M.; Driess, A.; Huttner, G.; Strähle, J. *Organometallics* **1999**, *18*, 598. Delgado, E.; Hernández, E.; Mansilla, N.; Moreno, M. T.; Sabat, M. *J. Chem. Soc., Dalton Trans.* **1999**, 533. Díez, J.; Gamasa, M. P.; Gimeno, J.; Aguirre, A.; García-Granda, S. *Organometallics* **1999**, *18*, 662. Onitsuka, K.; Yamamoto, S.; Takahashi, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 174. Jemmis, E. D.; Giju, K. T. *J. Am. Chem. Soc.* **1998**, *120*, 6952. George, D. S. A.; McDonald, R.; Cowie, M. *Organometallics* **1998**, *17*, 2553. Gu, X.; Sponsler, M. B. *Organometallics* **1998**, *17*, 5920. Schottek, J.; Erker, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **1998**, 551.

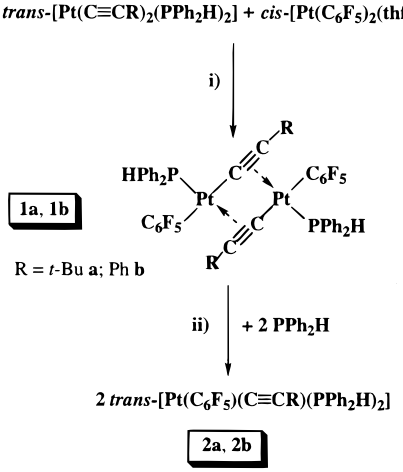
(2) (a) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E. *Inorg. Chim. Acta* **1997**, *264*, 199 and references therein. (b) Erker, G.; Albrecht, M.; Krüger, C.; Nolte, M.; Werner, S. *Organometallics* **1993**, *12*, 4979 and references therein. (c) Mihan, S.; Weidmann, T.; Weinrich, V.; Fenske, D.; Beck, W. *J. Organomet. Chem.* **1997**, *541*, 423 and references therein. (d) Yam, V. W.-W.; Lee, W.-K.; Cheung, K. K.; Lee, H.-K.; Leung, W.-P. *Chem. Commun.* **1996**, 2889. (e) Cuenca, T. M.; Gómez, R.; Gómez-Sal, P.; Rodriguez, G. M.; Royo, P. *Organometallics* **1992**, *11*, 1229. (f) Troyanov, S. I.; Varga, V.; Mach, K. *Organometallics* **1993**, *12*, 2820. (g) Ara, I.; Fernández, S.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5923. (h) Berenguer, J. R.; Forniés, J.; Martínez, F.; Cubero, J.; Lalinde, E.; Moreno, M. T.; Welch, A. J. *Polyhedron* **1993**, *12*, 797. (i) Ara, I.; Berenguer, J. R.; Eguizabal, E.; Forniés, J.; Lalinde, E.; Martín, A.; Martínez, F. *Organometallics* **1998**, *17*, 4578 and references therein.

10.1021/ic9900049 CCC: $18.00 © 1999 American Chemical Society
Published on Web 06/11/1999

$PhC{\equiv}CSiMe_3$, and the remaining PPh_2 fragment leads to the final heterobridged Ti−Ni mixed complex.

We are interested in these types of systems because phosphido and phosphinite bridges are very useful as strongly bound yet flexible ligands capable of stabilizing and maintaining the integrity of the binuclear fragments during chemical transformations.[9] Thus, it has been demonstrated that multisite-bound unsaturated ligands in binuclear phosphido-bridged complexes can be successfully derivatized with nucleophilic reagents, affording new C−C, C−N, C−P, or C−S bonds without destroying the μ-PR_2 bridge.[1b,7c,10] However, several recently reported transformations involving phosphido ligands set limits on their use for framework-stabilizing since they do not invariably behave as innocent bridging ligands.[11]

Scheme 1



Following our studies on the chemistry of alkynyl platinum complexes and phosphido polynuclear complexes, we are now exploring the possibilities of mixed phosphido−alkynyl or phosphinite−alkynyl bridges to stabilize heterobinuclear platinum complexes. With that purpose we have recently synthesized[12] heteroleptic platinum alkynyl complexes containing the acid ligands PPh_2H or PPh_2OH which can be used as precursors for bi- or polynuclear derivatives by simple deprotonation processes. We present here the conditions for the formation of a series of platinum−rhodium (μ-C≡CR)(μ-PPh_2) and platinum−rhodium and platinum−iridium (μ-C≡CR)(μ-PPh_2O) (R = *t*-Bu, Ph) dibridged complexes by reaction of *trans*-[Pt(C_6F_5)(C≡CR)-(PPh_2H)$_2$] (generated through the rupture of the homobridged *trans,sym*-[Pt(μ-κC^{α}:η^2-C≡CR)(C_6F_5)(PPh_2H)]$_2$ with PPh_2H), *cis*-[Pt(C≡CR)$_2$(PPh_2H)$_2$], and [Pt(C≡CR){(PPh_2O)$_2$H}(PPh_2-OH)] with rhodium or iridium acetylacetonate species [M(acac)-L_2] (L_2 = COD, M = Rh, Ir; L_2 = 2CO, M = Rh) (Scheme 2).

Results and Discussion

Heterobinuclear (μ-C≡CR)(μ-PPh_2) Complexes. Our initial efforts were concentrated on the use of the very stable platinum species *trans*-[Pt(C≡CR)$_2$(PPh_2H)$_2$][12] as precursors for the synthesis of heterobridged (μ-C≡CR)(μ-PPh_2) complexes. However, all of our attempts to synthesize heterobridged mixed

(3) (a) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376. (b) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628. (c) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618. (d) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3618. (e) Heeres, H. J.; Nijholf, J.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1993**, *12*, 2609. (f) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291. (g) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *14*, 5021. (h) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 2665. (i) Hsu, P. D.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 10394.

(4) (a) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112 and references therein. (b) Varga, V.; Mach, K.; Hiller, J.; Thewalt, U.; Sedmera, P.; Polásek, M. *Organometallics* **1995**, *14*, 1410.

(5) (a) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F.; Urriolabeitia, E.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1291 and references therein. (b) Werner, H.; Gevert, O.; Steinert, P.; Wolf, J. *Organometallics* **1995**, *14*, 1786. (c) Fritz, P. M.; Polborn, K.; Steimann, M.; Beck, W. *Chem. Ber.* **1989**, *122*, 889. (d) Silvestre, J.; Hoffman, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(6) (a) Ara, I.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Martín, A.; Martínez, F.; Moreno, M. T. *Organometallics* **1997**, *16*, 5392. (b) Miguel, D.; Moreno, M.; Pérez, J.; Riera, V. *J. Am. Chem. Soc.* **1998**, *120*, 417. (c) Takahashi, T.; Nishihara, Y.; Sua, W.-H.; Fisher, R.; Nakajima, K. *Organometallics* **1997**, *16*, 2216. (d) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. *Chem. Ber.* **1996**, *129*, 5. (e) Ipaktshi, J.; Mirzaei, F.; Mueller, B. G.; Beck, J.; Serafin, M. *J. Organomet. Chem.* **1996**, *526*, 363. (f) Lang, H.; Frosh, W.; Wu, I. Y.; Blau, S.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 6266. (g) Bruce, M. I.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *515*, 65. (h) Röttger, D.; Pflug, J.; Erker, G.; Kotila, S.; Fröhlich, R. *Organometallics* **1996**, *15*, 1265. (i) Röttger, D.; Erker, G.; Fröhlich, R. *Chem. Ber.* **1995**, *128*, 1045. (j) Cao, D. H.; Stang, P. J.; Arif, A. M. *Organometallics* **1995**, *14*, 2733. (k) Lai, N.-S.; Tu, W.−Ch.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1994**, *13*, 4652.

(7) (a) Smith, W. F.; Yule, J.; Taylor, N. J.; Paik, H. N.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 1593. (b) Cherkas, A. A.; Randall, L. H.; MacLaughlin, S. A.; Mott, G. N.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 969. (c) Blenkiron, P.; Corrigan, J. F.; Pilette, D.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2165. (d) Blenkiron, P.; Corrigan, J. F.; Pilette, D.; Taylor, N. J.; Carty, A. J. *Can. J. Chem.* **1996**, *74*, 2349. (e) Hogarth, G.; Redmond, S. P. *J. Organomet. Chem.* **1997**, *534*, 221. (f) Pulst, S.; Arndt, P.; Baumann, W.; Tillack, A.; Kempe, R.; Rosenthal, U. *J. Chem. Soc., Chem. Commun.* **1995**, 1753. (g) Carty, A. J.; Cherkas, A. A.; Randall, L. H. *Polyhedron* **1988**, *7*, 1045. (h) Doherty, S.; Elsegood, M. R. J.; Clegg, W.; Ward, M. F.; Waugh, M. *Organometallics* **1997**, *16*, 4251. (i) The mixed [FeRu(CO)$_6$(μ-κC^{α}:η^2-C≡C-*t*-Bu)(μ-PPh_2)] (δ(P) 137.6) has been also reported (ref 15, page 565). For M_4 species made up of two M(μ-C≡CR)(μ-PR_2)M see: (j) Daran, J.-C.; Jeannin, Y.; Kristiansson, O. *Organometallics* **1985**, *4*, 1882. (k) Blenkiron, P.; Enright, G. D.; Low, P. J.; Corrigan, J. F.; Taylor, N. J.; Chi, Y.; Saillard, J.-Y.; Carty, A. J. *Organometallics* **1998**, *17*, 2447. (l) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, C9.

(8) Fogg, D. E.; Taylor, N. J.; Meyer, A.; Carty, A. J. *Organometallics* **1987**, *6*, 2252.

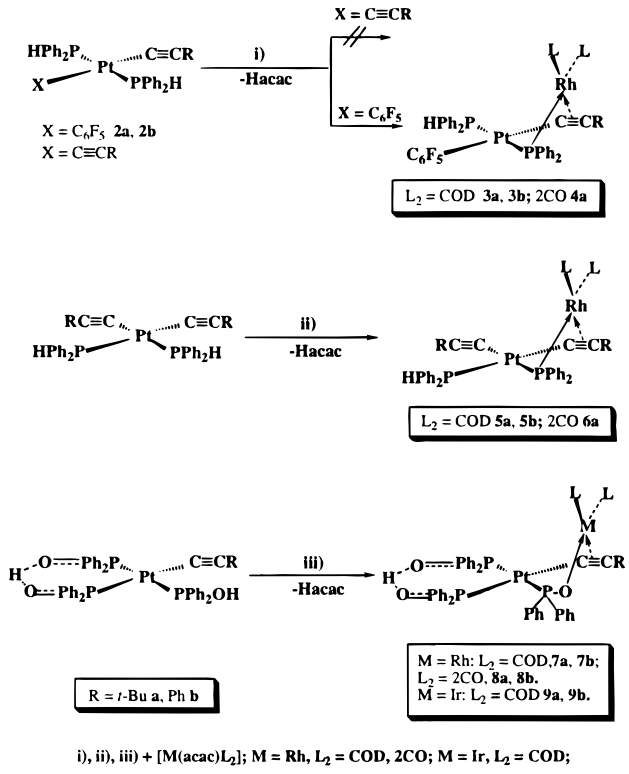
(9) (a) Leoni, P.; Pasquali, M.; Pieri, G.; Albinati, A.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1995**, *14*, 3143. (b) Braunstein, P.; de Jesús, E.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1992**, *31*, 411. (c) Powell, J.; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2793. (d) Leoni, P.; Pasquali, M.; Fortunelli, A.; Germano, G.; Albinati, A. *J. Am. Chem. Soc.* **1998**, *120*, 9564. (e) Shyu, S.-G.; Hsiao, S.-M.; Lin, K.-J.; Gau, H.-M. *Organometallics* **1995**, *14*, 4300. (f) Falvello, L. R.; Forniés, J.; Fortuño, C.; Martínez, F. *Inorg. Chem.* **1994**, *33*, 6242.

(10) (a) Cherkas, A. A.; Carty, A. J.; Sappa, E.; Pellinghelli, M. S.; Tiripicchio, A. *Inorg. Chem.* **1987**, *26*, 3201. (b) Cherkas, A. A.; Randall, L. H.; Taylor, N. J.; Mott, G. N.; Yule, J. E.; Guinamant, J. L.; Carty, A. J. *Organometallics* **1990**, *9*, 1677 and references therein. (c) Cherkas, A. A.; Doherty, S.; Cleroux, M.; Hogarth, G.; Randall, L. H.; Breckenridge, S. M.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 1701 and references therein. (d) Hogarth, G.; Lavender, M. H.; Shukri, K. *Organometallics* **1995**, *14*, 2325. (e) Carty, A. J.; Hogarth, G.; Enright, G.; Frapper, G. *Chem. Commun.* **1997**, 1883. (f) Chi, Y.; Carty, A. J.; Blenkiron, P.; Delgado, E.; Enright, G. D.; Wang, W.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1996**, *15*, 5269.

(11) (a) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1990**, *9*, 2234. (b) Brown, M. P.; Buckett, J.; Harding, M. M.; Lynden-Bell, R. M.; Mays, M. J.; Woulfe, K. W. *J. Chem. Soc., Dalton Trans.* **1991**, 307. (c) Etienne, M.; Mathieu, R.; Lugan, N. *Organometallics* **1993**, *12*, 140. (d) Falvello, L. R.; Forniés, J.; Fortuño, C.; Martín, A.; Martínez-Sariñena, A. P. *Organometallics* **1997**, *16*, 5849.

(12) (a) Falvello, L. R.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Sacristán, J. *Chem. Commun*. **1998**, 141. (b) Falvello, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Sacristán, J. *Chem.—Eur. J.* **1999**, *5*, 474.

Scheme 2



platinum compounds by deprotonation of *trans*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$] with [ML$_2$(acac)] (L$_2$ = COD, M = Rh, Ir; L$_2$ = 2CO, M = Rh) were unsuccessful. We have only found evidence of reaction for the systems R = *t*-Bu/[Rh(acac)COD] and R = Ph/[M(acac)L$_2$] (M = Rh, Ir, L$_2$ = COD, M = Rh, L = CO). However, the results of these reactions are not clear. The processes are very slow, and after prolonged reaction (~24 h), in all cases, substantial amounts of the starting materials are still present together with complex mixtures of undefined compounds as detected by NMR spectroscopy (^{31}P and ^{1}H).

Mononuclear platinum species of the type *trans*-[Pt(C$_6$F$_5$)(C≡CR)(PPh$_2$H)$_2$] (**2**), stabilized by two mutually trans PPh$_2$H ligands were next chosen as precursors. These complexes were prepared as shown in Scheme 1. By treating *trans*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$] [R = *t*-Bu (**a**), Ph (**b**)] with *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$] in CH$_2$Cl$_2$ at room temperature[2h,13] the binuclear complexes *trans,sym*-[Pt(μ-κC^{α}:η^2-C≡CR)(C$_6$F$_5$)(PPh$_2$H)]$_2$ (**1a**, **1b**) were obtained in moderate (62% **1a**) or low yield (42% **1b**); and in agreement with previous findings,[2h,13] treatment of complexes **1** with PPh$_2$H in CH$_2$Cl$_2$ results in bridge cleavage to give the desired mononuclear *trans*-[Pt(C$_6$F$_5$)(C≡CR)(PPh$_2$H)$_2$] (**2a**, **2b**).

These complexes are isolated as white (**1a**, **2a**) or beige (**1b**, **2b**) solids, the *tert*-butyl derivatives being more stable than the phenylethynyl homologues. The products were characterized by the usual means (Tables 1 and 2 and Experimental Section).

As shown in Scheme 2, step i (see Experimental Section), treatment of the resulting mononuclear complexes *trans*-[Pt(C$_6$F$_5$)(C≡CR)(PPh$_2$H)$_2$] (**2**) with 1 equiv of [Rh(acac)COD] in acetone at 20 °C readily afforded in good yields the heterobinuclear derivatives *trans,cis*-[(C$_6$F$_5$)(PPh$_2$H)Pt(μ-κC^{α}:η^2-C≡CR)(μ-PPh$_2$)RhCOD] (**3a**, **3b**) as orange microcrystalline solids. These solids are moderately air-stable, but in solution the products decompose in a few hours' time. The evolution of the reaction system **2**/[Rh(acac)(CO)$_2$] is more complicated due to the much slower formation of the analogous dimers **4** and especially because of their low stability in solution. Thus, monitoring by NMR spectroscopy indicates that the formation of **4a** in acetone at 20 °C needs approximately 48 h for completion. In that period a dark solution is formed, from which **4a** can be isolated only as an oily residue (with traces of impurity) which has been characterized spectroscopically in solution. However, the related phenylethynyl complex **4b** could not be obtained; the reaction between **2b** and [Rh(acac)(CO)$_2$] affords a complex mixture of products in which the expected **4b** could not be detected.

In contrast to the results with trans bis alkynyl derivatives described above, reactions involving the corresponding *cis*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$] substrates with [Rh(acac)L$_2$] in acetone at −20 °C resulted in the precipitation of *cis,cis*-[(C≡CR)(PPh$_2$H)Pt(μ-κC^{α}:η^2-C≡CR)(μ-PPh$_2$)RhL$_2$] [L$_2$ = COD, **5a** (orange), **5b** (yellow); L$_2$ = 2CO, **6a** (yellow)] in good yields (Scheme 2, ii). These complexes are moderately stable in the solid state (−30 °C), but seem to be very unstable in solution. Compound **6a** is always obtained with small amounts of the dinuclear derivative [Pt(C≡C-*t*-Bu)(μ-PPh$_2$)(PPh$_2$H)]$_2$[12b] as determined by NMR spectroscopy (^{1}H and ^{31}P{^{1}H}). Crystallization of the mixture at low temperature in different solvents gave yellow crystals of **6a** and white crystals of the binuclear product, which were separated by hand. Again, however, under similar reaction conditions the analogous phenylethynyl complex **6b** could not be obtained. In the reaction mixture only the precursor *cis*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$] and undefined rhodium−phosphine complexes were detected.

Attempts to prepare the iridium-containing binuclear analogues also failed. The NMR spectra (CDCl$_3$) of the mixture obtained by reacting **2** or *cis*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$] and 1 equiv of [Ir(acac)COD] reveal that the mononuclear complexes are always present in solution (after 24 h for **2a**, 12 h for **2b**, 4 h for cis *t*-Bu, 3 h for cis Ph), together with unidentified phosphine complexes. The relatively small amounts of these latter species and the very low stability of the reaction mixtures precluded their isolation and identification.

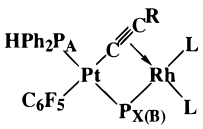
The heterobinuclear complexes **3**−**6** have been identified by IR and NMR spectroscopic techniques, mass spectrometry, and elemental analyses (except **4a**). Furthermore, the structure of **6a** was confirmed by X-ray crystallography (see below). Complexes **3** show in their IR spectra characteristic absorptions in the expected range for bridging alkynyl ligands, and in the cis alkynyl binuclear complexes, only **5b** shows a medium ν(C≡C) absorption at 2108 cm^{-1}, indicative of the presence of a terminal alkynyl ligand. The ν(CO) bands in complexes **4a** and **6a** appear in the same region as those observed in the starting material [Rh(acac)(CO)$_2$] [(2067, 2012 cm^{-1} (vs)], suggesting that the "Rh(CO)$_2$" fragment does not suffer significant electronic changes in the final products. The separation between the two bands ($\Delta\nu$ = 64 cm^{-1}, **6a**) is consistent with a cis formulation of the carbonyl ligands.[14]

Relevant ^{31}P{^{1}H} NMR data are given in Table 1. The spectra exhibit two well-separated signals with platinum satellites for all compounds. In each one, the resonance which appears at a position similar (δ −3.85 to −10.42) to that observed in the corresponding precursor is assigned to the secondary phosphine (P$_A$Ph$_2$H). This signal appears as a doublet [except **5b** (singlet)] with a bridge phosphorus coupling constant [^{2}J(P$_A$−P$_{X(B)}$)], as

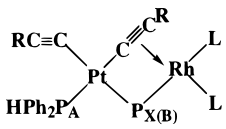
(13) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F.; Sanchez, L.; Serrano, B. *Organometallics* **1998**, *17*, 1640.

(14) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061.

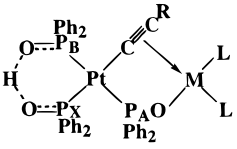
Table 1. $^{31}P\{^1H\}$ NMR in $CDCl_3$ at 20 °C for Complexes **3**−**9** (*J* in Hz), ^1J(Pt−P) in Brackets and ^1J(Rh−P) in Parentheses



for **3**, **4a**



for **5**, **6a**



for **7**, **8**, **9**

compound	δP_A	$\delta P_{X(B)}$	$^2J(P_A-P_{X(B)})$
3a, *trans*,*cis*-[$(C_6F_5)(PPh_2H)Pt(\mu$-κC^α:η^2-C≡C-*t*-Bu)(μ-PPh_2)RhCOD]	−5.80 (d) [2379]	36.75 (dd) [1720], (114)	328
3b, *trans*,*cis*-[$(C_6F_5)(PPh_2H)Pt(\mu$-κC^α:η^2-C≡CPh)(μ-PPh_2)RhCOD]	−8.76 (d) [2252]	0.1 [1720], (101)	326
4a, *trans*,*cis*-[$(C_6F_5)(PPh_2H)Pt(\mu$-κC^α:η^2-C≡C-*t*-Bu)(μ-PPh_2)Rh$(CO)_2$][a]	−10.42 (d) [2457]	21.57 (dd) [1697], (80)	339
5a, *cis*,*cis*-[(C≡C-*t*-Bu)$(PPh_2H)Pt(\mu$-κC^α:η^2-C≡C-*t*-Bu)(μ-PPh_2)RhCOD]	−3.85 (d) [2882]	−4.12 (dd) [1342], (99)	14.5
5b, *cis*,*cis*-[(C≡CPh)$(PPh_2H)Pt(\mu$-κC^α:η^2-C≡CPh)(μ-PPh_2)RhCOD]	−6.25 (s) [2701]	−46.95 (d) [1363], (105)	b
6a, *cis*,*cis*-[(C≡C-*t*-Bu)$(PPh_2H)Pt(\mu$-κC^α:η^2-C≡C-*t*-Bu)(μ-PPh_2)Rh$(CO)_2$]	−5.25 (d) [2793]	−14.26 (dd) [1364], (79)	18

	δP_A	δP_B	δP_X	$^2J(P_A-P_X)$	$^2J(P_B-P_X)$	$^2J(P_A-P_B)$
7a, [$\{(PPh_2O)_2H\}Pt(\mu$-κC^α:η^2-C≡C-*t*-Bu)(μ-$\kappa P,\kappa O$-PPh_2O)RhCOD]	73.88 [2120]	68.38 [2341]	74.63 [3044]	21.8	28.1	414
7b, [$\{(PPh_2O)_2H\}Pt(\mu$-κC^α:η^2-C≡CPh)(μ-$\kappa P,\kappa O$-PPh_2O)RhCOD]	76.68 [2151]	70.28 [2308]	74.56 [3002]	22.2	25.1	402
8a, [$\{(PPh_2O)_2H\}Pt(\mu$-κC^α:η^2-C≡C-*t*-Bu)(μ-$\kappa P,\kappa O$-PPh_2O)Rh$(CO)_2$][a]	79.65 [2104]	69.70 [2354]	72.59 [3049]	20.8	26.9	403
8b, [$\{(PPh_2O)_2H\}Pt(\mu$-κC^α:η^2-C≡CPh)(μ-$\kappa P,\kappa O$-PPh_2O)Rh$(CO)_2$][a]	81.34 [2144]	70.29 [2297]	72.40 [3024]	19.4	27.0	392
9a, [$\{(PPh_2O)_2H\}Pt(\mu$-κC^α:η^2-C≡C-*t*-Bu)(μ-$\kappa P,\kappa O$-PPh_2O)IrCOD]	78.38 [2086]	68.87 [2400]	71.55 [3077]	20.8	27.2	404
9b, [$\{(PPh_2O)_2H\}Pt(\mu$-κC^α:η^2-C≡CPh)(μ-$\kappa P,\kappa O$-PPh_2O)IrCOD]	94.14 [2285]	73.15 [2344]	73.12 [2938]	24.4	29.1	397

[a] Only characterized spectroscopically in solution. [b] It is not resolved.

expected, lower for the cis complexes (**5**−**6a**, 0−18 Hz) than for the trans (**3**−**4a**, 326−339 Hz). The other signal which is observed in complexes **5** and **6a** at lower frequencies (δ −4.12 to −46.95) and for complexes **3** and **4a** at higher frequencies (δ 0.1−36.75) is unambiguously assigned to the phosphido bridging groups ($P_{X,B}$) due to additional splitting by rhodium coupling, clearly lower in the dicarbonyl complexes [^1J(Rh−P) ∼ 80 Hz] than in the cyclooctadiene compounds (99−114 Hz, **3**, **5**). The chemical shifts of these μ-phosphido ligands[15] are in agreement with the platinum−rhodium separation of 3.142(1) Å found in the solid state for complex **6a**, which is approximately halfway between that expected for a conventional Pt(II)−Rh(I) bond[16] (strong deshielding) and that for a nonbonding distance (P resonance significantly shielded). Comparison of the values of the ^1J(Pt−P) coupling constants suggests that the bridging phosphido ligand exerts a larger trans influence than the alkynyl bridging ligand [$^1J(Pt-P_A)$ 2252−2457, **3**, **4a**, vs 2701−2882, **5**, **6a**] and that the terminal alkynyl possesses a stronger trans influence than does PPh_2H [$^1J(Pt-P_X)$ 1342−1364 Hz, **5**, **6a**, *vs* $^1J(Pt-P_X)$ 1697−1720 Hz in **3**−**4a**]. The terminal P−H protons in these complexes give rise to ^1H NMR signals (dd) ranging from 5.12 to 6.52 ppm, which show coupling to phosphorus nuclei [AMX system, $^1J(P_A-H)$ 370−385 Hz, $^3J(P_X-H)$ 3.0−16.7 Hz] and an additional Pt−H coupling in the range 27−35 Hz. The asymmetry of the μ-C≡CR/μ-PPh_2 system is inferred from the COD (^1H and ^{13}C) resonances in **3** and **5** (see Table 2 and Experimental Section). Notwithstanding, the proton spectra display (even at low temperature) only two olefinic resonances, clearly suggesting the existence of a fluxional process (presumably a rapid ring inversion of the central metallacycle) which would average the endo and exo protons of the diolefin.

The low-temperature (−50 °C) ^{19}F NMR spectrum (see Experimental Section) of **3a** shows that the five fluorine atoms of the C_6F_5 ligand are inequivalent, confirming not only the bent conformation of the Pt(μ-C≡CR)(μ-PPh_2)Rh core (as observed in solid state for **6a**) but also that the rotation of the C_6F_5 groups is hindered. At higher temperatures, the two ortho fluorine signals (as well the two meta fluorine signals) collapse to give broad unresolved signals (at +20 °C) or sharp signals (at +50 °C), suggesting dynamic behavior. At 20 °C, compounds **3b** and **4a** exhibit (**3b** even at −50 °C) the same pattern as **3a** at high temperature. Since the platinum fragment is rather similar in the three complexes,[17] this further suggests that the equivalence of ortho and meta fluorine atoms is attained by means of a rapid intramolecular inversion of the central metallacycle.

$^{13}C\{^1H\}$ analyses for **3b** and **4a** were rendered impossible by low solubility (**3b**) or low stability (**4a**). For the rest of the complexes the most useful information comes from the C_α and C_β alkynyl carbon resonances which appear in the expected range (δ C_α/C_β 73.6−103.2/111.7−122.4). Although ^{195}Pt

(15) Carty, A. J.; McLaughlin, S. A.; Nucciarone, D. in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 8, Chapter 16. See also refs 18−22.
(16) Tanase, T.; Toda, H.; Kobayashi, K.; Yamamoto, Y. *Organometallics* **1996**, *15*, 5272 and references therein.
(17) It should be noted that the equivalence of the two halves of the C_6F_5 ligand can also be achieved by a free rotation of this group about the Pt−C_{ipso} linkage. However, in these species, the rotation of the C_6F_5 ligand is expected to have similar energetic barriers in the three complexes: Casares, J. A.; Espinet, P.; Martínez-Ilarduya, J. M.; Lin, Y.-S. *Organometallics* **1997**, *16*, 770.

Table 2. ^{1}H NMR Data[a] for the Complexes (J in Hz)

compd	T[a] (°C)	δ(*t*-Bu)	δ(PPh$_2$H)	^1J(P−H)[b]	^3J(P−H)	δ(O···H···O)	δ(Ph)	δ(COD) ═CH	δ(COD) CH$_2$
1a	20	0.65 (s, 18H)	6.35 (d, 2H)	∼408 [38]			7.72 (m, 8H), 7.39 (m, 12H)		
1b	20		*c*	*c* [46]			7.78 (m, 4H), 7.39−6.67 (m, 26H)		
2a	20	0.89 (s, 9H)	6.42 (2H)[d]	d			7.68 (br, 8H), 7.33 (br, 12H)		
2b	20		*c*	*c*			7.68−6.88 (m, 25H)		
3a	20	0.88 (s, 9H)	6.26 (dd, 1H)	370 [33]	3.0		7.71 (m, 4H), 7.36 (m, 10H), 7.16 (m, 6H)	4.62 (s, 2H), 3.95 (br, 2H)	2.24 (br, 4H), 1.96 (br, 4H)
	−50	0.85 (s, 9H)	*c*	*c*	*c*		7.87, 7.59, 7.37, 6.90 (br)	4.43 (br, 3H), 3.31 (br, 1H)	2.5, 1.9 (vbr), 1.5 (br)
3b	20		*c*	*c*	12		7.75−6.84 (m, 25H)	4.42 (s, 2H), 3.78 (s, 2H)	2.35, 2.16, 2.04, 1.8
	−50		*c*	*c*	*c*		7.67−6.79 (m, 25H)	4.36 (s, br, 2H), 3.57 (s, br, 2H)	2.35, 2.19, 2.04, 1.93
4a[e]	20	0.96 (s, 9H)	6.52 (dd, 1H)	385 [35]	4.6		7.84, 7.57, 7.30 (m, 20H)		
5a	20	1.11 (s, br, 18H)	5.48 (dd, 1H)	375 [28]	14.9		7.88 (m, 4H), 7.34 (m, 10H), 7.15 (m, 6H)	5.45 (br, 2H), 3.61 (br, 2H)	2.26 (br, 4H), 1.99 (br, 4H)
	−50	1.15 (s, 9H) 1.11 (s, 9H)	5.43 (dd, 1H)	376 *f*	15		7.86 (m, 4H), 7.37 (m, 10H), 7.20 (m, 6H)	5.53 (s, 2H), 3.36 (br, 2H)	2.23 (m, 4H), 1.99 (m, 4H)
	+50	1.12 (s, 9H) 1.11 (s, 9H)	5.51 (dd, 1H)	376 [27]	14.3		7.89 (m, 4H), 7.35 (m, 10H), 7.14 (m, 6H)	5.43 (s, 2H), 3.71 (br, 2H)	2.26 (m, 4H), 2.01 (m, 4H)
5b	20		5.62 (dd, 1H)	376 [31.5]	16.1		7.88 (m, 4H), 7.52 (m, 4H), 7.36 (m, 6H), 7.12 (m, 16H)	4.68 (s, br, 2H), 3.42 (s, br, 2H)	2.27 (m, 4H), 1.98 (m, 4H)
	−50		5.61 (dd, 1H)	377 *f*	15.9		7.87 (m, 4H), 7.52 (m, 4H), 7.38 (m, 6H), 7.19 (m, 16H)	4.58 (s, 2H), 3.28 (s, 2H)	2.34 (br, 4H), 1.95 (br, 4H)
6a	20	1.11 (s, 9H), 1.08 (s, 9H)	5.12 (dd, 1H)	379 [28]	16.7		7.67 (m), 7.21−7.48 (m), 7.09 (m, 20H)		
7a	20	1.08 (s, 9H)				17.2 (br)	8.26 (m, 2H), 8.12 (m, 2H), 7.55−7.21 (m, 18H), 7.01 (m), 6.94 (m) (4H), 6.62 (m, 2H), 6.46 (m, 2H)	4.86 (m, 1H), 4.32 (m, 1H), 3.18 (m, 1H)	2.64 (m, 2H),[g] 2.46 (m, 1H), 2.19 (m, 1H), 1.97 (m, 2H), 1.79 (m, 1H), 1.45 (m, 1H), 1.35 (m, 1H)
7b	20					15.5 (br)	7.77, 7.55, 7.34, 7.05, 6.61 (m, 35H)	4.67 (s, br, 1H), 2.57 (s, br, 1H)[h]	2.39 (m, 2H), 2.07 (m, 2H), 1.74 (m, 2H), 1.53 (m, 2H), 1.25 (m, 1H), 0.86 (m, 1H)
8a[e]	20	0.83 (s, 9H)				*f*	7.97−6.96 (m), 6.7 (t), 6.49 (t) (30H)		
8b[e]	20					15.5 (br)	7.84 (m, 3H), 7.6−7.05 (m, 30H), 7.86 (d, 2H)		
9a	20	1.01 (s, 9H)				*f*	8.17 (m), 8.06 (m), 7.53−6.52 (m) (30H)	4.73 (s, br, 1H), 4.00 (s, br, 1H), 2.99 (s, br, 1H), 2.79 (s, br, 1H)	2.20 (m, 2H), 1.84 (m, 2H), 1.49 (m, 2H), 1.24 (m, 2H)
9b	20					*f*	7.53 (m), 7.38−7.07 (m), 6.81 (m) (35H)	4.35 (s, 1H), 3.74 (s, 2H), 2.53 (s, 1H)	2.23, 1.97, 1.84, 1.54 (m, 8H)

[a] In $CDCl_3$, chemical shifts are reported relative to $SiMe_3$ as external reference. [b] $^2J_{^{195}Pt-H}$ in brackets. [c] The δ(PPh$_2$*H*) and ^1J(P−H) cannot be determined even with a $^1H\{^{31}P\}$ NMR experiment for **1b** and **2b**. [d] AA′XX′ system, $N = {}^1J(P-H) + {}^3J(P'-H) = 392.5$ Hz. [e] Only characterized spectroscopically in solution. [f] Not observed. [g] 2 H, 1 CH_2, + 1 ═CH. [h] Two olefinic protons overlap in the CH_2 region.

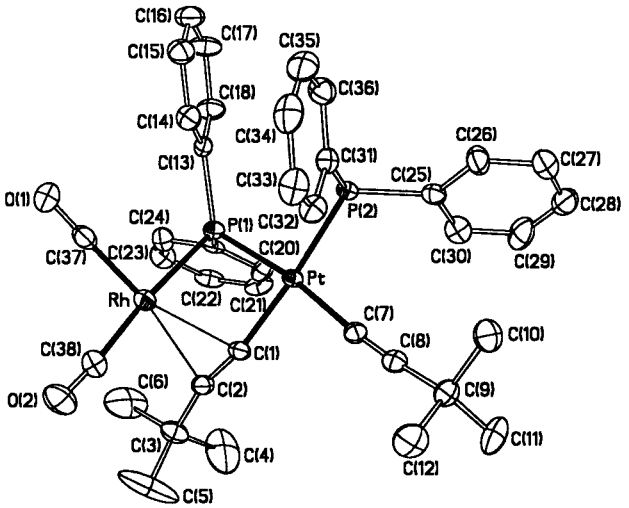


Figure 1. Molecular structure of *cis,cis*-[(C≡C-*t*-Bu)(PPh_2H)Pt(μ-κC^{α}:η^2-C≡C-*t*-Bu)(μ-PPh_2)Rh($CO)_2$] (**6a**) showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

satellites are not observed, C_α or C_β resonances can be assigned unambiguously on the basis of carbon-trans and carbon-cis phosphorus coupling constants. The assignment as C_α/C_β terminal or bridging has been tentatively carried out by assuming larger coupling of μ-$C_\alpha{\equiv}C_\beta R$ to terminal P_A than of terminal σ-$C_\alpha{\equiv}C_\beta R$ to bridging P_X. With this assumption in mind, we observe small upfield shifts for C_α signals relative to the precursors [*cis*-[Pt(C≡CR)$_2$(PPh_2H)$_2$] δC_α 84.3 (R = *t*-Bu); 99.9 (R = Ph)] upon η^2 coordination of the C≡CR ligands to rhodium, as was previously found for related complexes.[2i,18] For **6a**, the two CO signals [trans (δ 186.1) and cis (δ 185.0) to μ-PPh_2^-] could be easily identified due to their significantly different coupling constants to the rhodium and phosphorus centers [^1J(C−Rh)/^2J(C−P) 58.8/92.6 trans to μ-P, 78.9/10.8 cis to μ-P]. Again, comparison of ^1J(Rh−C) confirms that the bridging μ-PPh_2 group exerts a larger trans influence than does the μ-C≡C-*t*-Bu (η^2-bonded).

The structure of **6a** was established by an X-ray diffraction study (see Figure 1 and Table 3). As was deduced on the basis of NMR studies, the molecule possesses a central folded Pt(μ-C≡C-*t*-Bu)(μ-PPh_2)Rh core. The platinum atom completes its usual square planar coordination with one PPh_2H molecule and one C≡C-*t*-Bu terminal group. The geometry about the rhodium(I) is also essentially square planar with the remaining two coordination sites being occupied by two carbonyl ligands. The dihedral angle formed by the corresponding metal coordination planes is 71.6°. The stabilization of the Rh(μ-PPh_2)($CO)_2$ fragment with a square planar coordination at the Rh(I) center on the binuclear species is particularly significant.[19] It has been previously noted that the tendency of the Rh center in the Rh(μ-PPh_2)($CO)_2$ unit to adopt a tetrahedral geometry is presumably the reason for its giving rise to a number of oligomeric products of the types [Rh_3(μ-PPh_2)$_3$($CO)_n$] (n = 5, 7, 9) and [Rh_4(μ-PPh_2)$_4$($CO)_6$].[19a] The simple dimer [Rh(μ-PPh_2)($CO)_2$]$_2$ is not known, and as far as we know, the most closely related species structurally characterized are the two isomers of [Rh(μ-P*t*-Bu$_2$)($CO)_2$]$_2$ (**A** and **B**).[20] In one isomer (**A**) both rhodium atoms retain the normal four-coordinate planar coordination geometry with no metal−metal bond [Rh···Rh 3.717(1) Å] while in the other isomer one rhodium is planar and the other is tetrahedral and the dimer has a Rh−Rh distance of 2.761 Å, consistent with the presence of a single Rh−Rh bond.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex *cis,cis*-[(C≡C-*t*-Bu)(PPh_2H)Pt(μ-κC^{α}:η^2-C≡C-*t*-Bu)-(μ-PPh_2)Rh($CO)_2$] (**6a**)

Pt(1)−C(1)	2.012(5)	Pt−C(7)	2.014(6)
Pt−P(2)	2.256(2)	Pt−P(1)	2.297(1)
Pt−Rh	3.142(1)	Rh−C(37)	1.830(6)
Rh−C(38)	1.925(7)	Rh−C(1)	2.312(6)
Rh−P(1)	2.323(2)	Rh−C(2)	2.418(6)
O(1)−C(37)	1.138(7)	O(2)−C(38)	1.125(7)
C(1)−C(2)	1.216(8)	C(7)−C(8)	1.192(8)
C(1)−Pt-C(7)	95.5(2)	C(1)−Pt-P(2)	175.5(2)
C(7)−Pt-P(2)	87.5(2)	C(1)−Pt-P(1)	77.4(2)
C(7)−Pt-P(1)	171.2(2)	P(2)−Pt-P(1)	99.4(1)
C(37)−Rh-C(38)	92.9(3)	C(37)−Rh-P(1)	91.4(2)
C(1)−Rh-P(1)	71.3(1)	Pt−P(1)−Rh	85.7(1)
C(38)−Rh-C(1)	103.5(2)	C(38)−Rh-C(2)	88.1(2)
Pt−C(1)−C(2)	167.9(5)	C(1)−C(2)-C(3)	164.5(6)
Pt−C(1)−Rh	92.9(2)	C(8)−C(7)-Pt	173.5(5)
C(7)−C(8)-C(9)	174.9(6)		

The platinum−rhodium distance [3.142(1) Å] in **6a** is clearly longer, and the angle at the bridging phosphorus atom [85.71-(5)°] is rather less acute than those found for conventional Pt−Pt or Rh−Rh metal−metal bonds supported by *closed* M(μ-PPh_2)M bridge bonding[11d,19a,20,21] (i.e., [Pt_4(μ-PPh_2)$_4$(C_6F_5)$_4$($CO)_2$], Pt(3)−Pt(2,4) 2.699(1), 2.688(1) Å; Pt−P−Pt 71.9(1)−73.5-(1)°;[11d] [(PEt_3)$_2$Rh(μ-PPh_2)$_2$RhCOD], Rh−Rh 2.752(1), Rh−P−Rh 73.4(1), 74.16(4)° [21a]). However, the distance is still markedly shorter than those expected for a complete nonbonding metal−metal interaction[20,22] (i.e., [Pt(C≡C-*t*-Bu)(μ-PPh_2)-(PPh_2H)]$_2$, Pt···Pt 3.649(1) Å, P−Pt−P 103.2(1)°;[12b] [Rh(μ-PPh_2)(dppe)]$_2$, Rh···Rh 3.471(1) Å, Rh−P−Rh 94.7(1)° [22a]). In fact, similar PPh_2 bridged metal−metal (Pt···Pt or Rh···Rh) distances were considered as intermediate between bonding and nonbonding in triplatinum[21c] and trirhodium[19a] clusters, with angles at the phosphorus atom ranging from 81.1(1)° to 89.0-(1)°.

In comparison with other alkynyl platinum−rhodium systems, the Pt(II)−Rh(I) bond length [3.142(1) Å] in **6a** is clearly longer than that found in [(PPh_3)$_2$Pt(μ-H)(μ-κC^{α}:η^2-C≡CPh)RhCp*-(PMe_3)]$^{2+}$ [2.826(1) Å][6j] but shorter than those observed for neutral Pt(II)−Rh(III) systems such as [(PEt_3)Cp*Rh(μ-κC^{α}:η^2-C≡C-*t*-Bu)(μ-Cl)Pt(C_6F_5)$_2$] [3.371(1) Å] or [(PEt_3)Cp*Rh-(μ-κC^{α}:η^2-C≡CSiMe_3)(μ-2κC^{α}:η^2-C≡CSiMe_3)Pt(C_6F_5)$_2$] [3.554-(1) Å].[2i]

The M−P (phosphido) distances [Pt−P = 2.297(1) Å, Rh−P = 2.323(2) Å] are comparable to those reported for related complexes.[11d,19−22] The alkynyl ligand bridges the metal centers

(18) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E. *Organometallics* **1997**, *16*, 3921.
(19) (a) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Dalton Trans.* **1984**, 515. See also: (b) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.
(20) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 470.
(21) (a) Meek, D. W.; Kreter, P. E.; Christoph, G. G. *J. Organomet. Chem.* **1982**, *231*, C53. (b) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Orpen, G. *Chem. Commun*. **1996**, 231. (c) Bender, R.; Braunstein, P.; Dedieu, A.; Ellis, P. D.; Huggins, B.; Harvey, P. D.; Sappa, E.; Tiripicchio, A. *Inorg. Chem.* **1996**, *35*, 1223. (d) Leoni, P.; Manetti, S.; Pasquali, M.; Albinati, A. *Inorg. Chem*. **1996**, *35*, 6045. (e) Jones, R. A.; Wright, T. C. *Organometallics* **1983**, *2*, 1842.
(22) (a) Fultz, W. C.; Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem*. **1983**, *22*, 860. (b) Forniés, J.; Fortuño, C.; Navarro, R.; Martínez, F.; Welch, A. J. *J. Organomet. Chem.* **1990**, *394*, 643. (c) Kourkine, I. V.; Chapman, M. B.; Gluek, D. S.; Eichele, K.; Wasylishen, R. E.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem*. **1996**, *35*, 1478 and references therein. (d) Alonso, E.; Forniés, J.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton Trans*. **1995**, 3777.

in the most commonly observed $\sigma-\pi$-mode in which the α-C atom is bonded to platinum [Pt−C 2.012(5) Å] and the unsaturated C≡C bond is unsymmetrically η^2-bonded to the rhodium center [Rh−C(1) 2.312(6), Rh−C(2) 2.418(6) Å]. The two C≡C distances are identical within experimental error [C(1)≡C(2) = 1.216(8) Å, C(7)≡C(8) = 1.192(8) Å]. As expected, there is a marked deviation from linearity in the alkynyl bridging group, with angles at C_α and C_β 167.9(5)°/164.5(6)° smaller than in the alkynyl terminal group 173.5(5)°/174.9(6)°.

The Rh−CO distance trans to the C≡C triple bond [Rh−C(37) 1.830(6) Å] is significantly shorter than the corresponding distance trans to the phosphido ligand [Rh−C(38) 1.925(7) Å], reflecting not only the asymmetric disposition of the bridging ligands but also the stronger trans influence of the phosphido ligand, in keeping with the NMR data (see above).

Heterobinuclear (μ-C≡CR)(μ-PPh_2O) Derivatives. Recently[12b] we have described the synthesis of unusual mononuclear alkynyl−phosphinite complexes of the type [Pt(C≡CR)-{$(PPh_2O)_2H$}(PPh_2OH)] stabilized by two molecules of hydroxyphosphine; and we have shown that these complexes can be totally deprotonated by lithium hydroxide, yielding unusual sandwiched [Pt(C≡CR)$(PPh_2O)_3Li_2(H_2O)(THF)]_2$ compounds formed by self-assembly of the resulting (alkynyl)tris(diphenylphosphinite)platinate(II) fragments with the lithium ions. For comparative purposes, we have now studied the reactivity of these hydroxy phosphine complexes toward the [M(acac)L_2] substrates. As is summarized in Scheme 2, step iii, treatment of [Pt(C≡CR){$(PPh_2O)_2H$}(PPh_2OH)], in acetone (R = *t*-Bu) or thf (R = Ph), at low temperature (−20 °C) with 1 equiv of [M(acac)L_2] [M = Rh, Ir; L_2 = COD, $(CO)_2$] results in the formation of binuclear complexes [{$(PPh_2O)_2H$}Pt(μ-κC^α:η^2-C≡CR)(μ-κP,κO-PPh_2O)ML_2] (M = Rh, L_2 = COD, **7a**, **7b**; L_2 = 2CO, **8a**, **8b**; M = Ir, L_2 = COD, **9a**, **9b**) in moderate to good yield (59−73%). The cyclooctadiene complexes are isolated as solids (yellow/orange) after the usual workup. However, complexes **8a** and **8b** are extremely soluble even in solvents such as *n*-hexane, pentane, or diethyl ether and hence the final oily residues (pure **8a** and **8b** by ^{31}P NMR) are only characterized spectroscopically.

Attempts at growing suitable crystals of any of these heterobridged (μ-C≡CR)(μ-PPh_2O) complexes **7**−**9** for an X-ray analysis were unsuccessful. However, their characterization by microanalysis (except **8**), spectroscopic means (IR, NMR, see Tables 1 and 2), and mass spectrometry is straightforward; the lack of solubility for **7b** and **9** and stability for **8** prevented their identification by ^{13}C NMR spectroscopy. All complexes show the expected peak corresponding to the molecular ion in their FAB(+) mass spectra together with peaks derived from the loss of the COD ligand or M(COD) fragment as well as the Pt{$(PPh_2O)_2H$} unit (**7a**, **7b**, **9a**). Their IR spectra showed absorptions in the P−O stretching region (range 1029−962 cm^{-1}), and the lack of bands due to ν(O−H) in the normal region is consistent with the presence of symmetrical hydrogen bond formation as has been previously described.[12b,23] Complexes **7** and **8b** clearly exhibit in their ^{1}H NMR at 20 °C a broad downfield signal (δ 15.5−17.2**)**, confirming the presence of strong O···H···O hydrogen bonds.[12b,23b,24] Although the presence of an alkynyl bridging ligand is only observed in the IR spectrum of **9b** (2019 cm^{-1}), the ^{1}H NMR spectra of *tert*-butyl derivatives exhibit the expected singlet due to C≡C-*t*-Bu with the appropriate integration ratio. The presence of a central bent core is unambiguously inferred from the asymmetry of the COD ligand in solution. Thus, complexes **9** clearly display at 20 °C four nonequivalent olefinic and four aliphatic signals in the proton spectra. In complexes **7**, although is not possible to assign separately the olefinic and aliphatic protons because these overlap each other, the integration is correct for the 12 protons. Similarly, ^{13}C{^{1}H} NMR spectroscopy at −50 °C on **7a** reveals four olefinic doublet resonances produced by coupling to ^{103}Rh [δ range 89.9−69.1; J(C−Rh) 14.2−10.9 Hz] and four singlet signals for the aliphatic carbons (δ 34.3−27.3). The η^2-bonded alkyne signals at 86.9 ppm (C_α) and 113.4 (C_β) are seen as doublets of multiplets although the ^{195}Pt satellites are not observed despite prolonged accumulation.

All complexes display in their ^{31}P{^{1}H} NMR spectra the expected ABX pattern with platinum satellites. The signal due to the central phosphorus atom trans to μ-C≡CR (range 71.55−74.63) appears as a triplet due to similar *cis* $^2J(P_X-P_{A,B})$ (19.4−29.1 Hz) coupling and is easily identified. The remaining P_A (73.88−94.14) and P_B (68.38−73.15) signals due to mutually trans phosphorus atoms exhibit a dd splitting pattern with a large two-bond trans P_A-P_B coupling (392−414 Hz). The high-frequency signal, which experiences larger shifts upon changing the ML_2 unit (i.e., δ 73.88, **7a**, vs δ 79.65, **8a**) is tentatively assigned to the phosphinite bridging ligand (P_A); and the low-frequency signal, which appears closer to P_X, is assigned to the other phosphorus atom of the mixed chelating $PPh_2O-H\cdots OPPh_2$ system.

In summary, the reactivity of several mononuclear alkynyl platinum complexes stabilized by acidic molecules (PPh_2H or PPh_2OH) toward deprotonating metal complexes [M(acac)L_2] (M = Rh, Ir) has been studied. We have found that only the σ-alkynyl complexes *trans*-[Pt(C_6F_5)(C≡CR)$(PPh_2H)_2$] (**2**), *cis*-[Pt(C≡CR)$_2(PPh_2H)_2$], and [Pt(C≡CR){$(PPh_2O)_2H$}(PPh_2OH)] (R = *t*-Bu, Ph) are suitable precursors for heterobridged (μ-C≡CR)(μ-X) (X = PPh_2, PPh_2O) derivatives through simple deprotonation processes. In addition, formation of either heterobridged rhodium or iridium−platinum binuclear complexes [{$(PPh_2O)_2H$}Pt(μ-κC^α:η^2-C≡CR)(μ-κP,κO-PPh_2O)ML_2] (**7**−**9**) is only straightforward starting from [Pt(C≡CR){$(PPh_2O)_2H$}-(PPh_2OH)]. The reactions of the platinum precursors containing PPh_2H with the rhodium or iridium acetylacetonate complexes [M(acac)L_2] greatly depend on the nature of the metal, the ligands, and the alkynyl organic substituent R. Thus, only the expected heterobridged binuclear Pt−Rh complexes [X(PPh_2H)-Pt(μ-κC^α:η^2-C≡CR)(μ-PPh_2)RhL_2] [X = C_6F_5 (**3**, **4a**), C≡CR (**5**, **6a**) can be isolated starting from [Rh(acac)L_2]. The influence of the alkynyl substituent seems to be decisive in the final stability of the dimers (C≡C-*t*-Bu > C≡CPh), and in the case of L = CO, only when R = *t*-Bu are the final complexes easily formed (**4a**, **6a**). The structure of *cis*,*cis*-[(C≡C-*t*-Bu)(PPh_2H)-Pt(μ-κC^α:η^2-C≡C-*t*-Bu)(μ-PPh_2)$Rh(CO)_2$] (**6a**) has been solved by an X-ray diffraction study, and to our knowledge, this is just the second report of a heterobimetallic complex stabilized by a (μ-C≡CR)(μ-PPh_2) bridging system.

(23) (a) Roundhill, D. M.; Sperline, R. P.; Beaulieu, W. B. *Coord. Chem. Rev.* **1978**, *26*, 263. (b) Carty, A. J.; Jacobson, S. E.; Simpson, R. T.; Taylor, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 7254. (c) Dixon, K. R.; Rattray, A. D. *Can. J. Chem.* **1971**, *49*, 3997. (d) Cornock, M. C.; Gould, R. O.; Jones, C. L.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1307.

(24) See: R. F.; Curtis, Ch. J.; McConnell, K. W.; Santhanam, S.; Strub, W. M.; Ziller, J. W. *Inorg. Chem.* **1997**, *36*, 4151 and references therein.

Experimental Section

General methods and instrumentation have been described previously.[12b] The starting materials *trans,cis*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$], [Pt(C≡CR){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (R = *t*-Bu, Ph),[12b] *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$],[25] [Rh(acac)(CO)$_2$],[26a] and [M(acac)(COD)][26b,c] (M = Rh, Ir) were prepared as described elsewhere.

Preparation of *trans,sym*-[Pt(μ-κC$^\alpha$:η^2-C≡CR)(C$_6$F$_5$)(PPh$_2$H)]$_2$ (R = *t*-Bu, 1a; R = Ph, 1b). A colorless solution of *trans*-[Pt(C≡C-*t*-Bu)$_2$(PPh$_2$H)$_2$] (0.401 g, 0.549 mmol) in CH_2Cl_2 (15 mL) was treated with 0.370 g (0.549 mmol) of *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$], and the resulting yellow solution was stirred for 20 min. Then, the solvent was evaporated to a small volume (ca. 2 mL) and treated with cold ethanol (∼5 mL) to give 0.297 g of complex **1a**. Concentration of the mother liquors and cooling to −30 °C afforded an additional fraction (0.133 g, 62% yield).

The phenyl complex **1b** was prepared in a similar way using the appropriate starting materials *trans*-[Pt(C≡CPh)$_2$(PPh$_2$H)$_2$] (0.400 g, 0.520 mmol) and *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$] (0.350 g, 0.520 mmol) (0.0288 g, 42% yield).

1a. Anal. Calcd for $C_{48}F_{10}H_{40}P_2Pt_2$: C, 45.80; H, 3.20. Found: C, 45.50; H, 3.14. MS: *m*/*z* 1089 ([M − C$_6$F$_5$ − 2]$^+$, 24), 1007 ([M − C$_6$F$_5$ − C≡C-*t*-Bu − 3]$^+$, 16), 922 ([M − 2C$_6$F$_5$ − 2]$^+$, 19), 842 ([M − 2C$_6$F$_5$ − C≡C-*t*-Bu − 1]$^+$, 15), 760 ([Pt$_2$(PPh$_2$)$_2$]$^+$, 29), 681 ([Pt$_2$(PPh$_2$)PPh − 2]$^+$, 63), 629 ([M/2]$^+$, 24), 604 ([Pt$_2$(PPh$_2$)P − 2]$^+$, 100), 528 ([Pt(C$_6$F$_5$)$_2$ − 1]$^+$, 73), 377 ([PtPPh$_2$ − 3]$^+$, 25). IR (ν_{max}/cm^{-1}): a weak band at 2310 was tentatively assigned to PH, 2007 (m) (C≡C), 786 (s) (C$_6$F$_5$)$_{X-sens}$. ^{19}F NMR at 20 °C: δ −116.2 [d, F$_o$, ^3J(Pt−F$_o$) = 263], −161.6 (t, F$_p$), −164.3 (m, F$_m$). A similar pattern was observed at −50 °C: −116.5 [d, br, F$_o$, ^3J(Pt−F$_o$) = 250], −160.7 (t, F$_p$), −163.5 (br, F$_m$).^{13}C{^{1}H} NMR at 20 °C: δ 147.3 [dd, ^1J(C−F) ∼ 231, ^2J(C−F) ∼ 16.8, C$_6$F$_5$], 136.8 (dm, "*J*" ∼ 235, C$_6$F$_5$), 133.3 [d, ^2J(C−P) = 11.1, C$_o$, PPh$_2$H], 130.9 (s, C$_p$, PPh$_2$H), 128.05 [d, ^3J(C−P) = 11.6, C$_m$, PPh$_2$H], 127.5 [d, ^1J(C−P) = 67.9, C$_{ipso}$, PPh$_2$H], 121.4 [d, *J*(C−P) = 21.6], 87.5 (m) (Cα,Cβ, Pt satellites are not observed), 31.1 [s, br, C(*C*H$_3$)$_3$], 30.2 (s, *C*Me$_3$). ^{31}P{^{1}H}NMR: δ −12.93, ^1J(Pt−P) = 3866.

1b. Anal. Calcd for $C_{52}F_{10}H_{32}P_2Pt_2$: C, 48.08; H, 2.48. Found: C, 48.50; H, 2.78. MS: *m*/*z* 1220 ([M − Ph]$^+$, 20), 1130 ([M − C$_6$F$_5$]$^+$, 15), 798 ([Pt(C$_6$F$_5$)$_2$(C≡CPh)(PPh$_2$H) − F]$^+$, 45), 719 ([Pt(C$_6$F$_5$)$_2$(C≡CPh)(PPh) − F − 1]$^+$, 100), 603 ([Pt$_2$(PPh$_2$)P − 3]$^+$, 40), 529 ([Pt(C$_6$F$_5$)$_2$]$^+$, 35), 377 ([PtPPh$_2$ − 3]$^+$, 85). IR (ν_{max}/cm^{-1}): 2345 (w) (tentatively assigned to PH), 2020 (w) (C≡C), 799 (s) (C$_6$F$_5$)$_{X-sens}$. ^{19}F NMR at 20 °C: δ −118.3 [dm, F$_o$, ^3J(Pt−F$_o$) = 254], −161.9 (t, F$_p$), −164.4 (m, F$_m$). The ^{13}C NMR spectrum could not be recorded due to the very low stability of **1b** in solution. ^{31}P{^{1}H}NMR: δ −13.45, ^1J(Pt−P) = 3827.

Preparation of *trans*-[Pt(C$_6$F$_5$)(C≡CR)(PPh$_2$H)$_2$] (R = *t*-Bu, 2a; R = Ph, 2b). (PPh$_2$H 120 μL, 0.659 mmol) was added to a solution of *trans,sym*-[Pt(μ,κC$^\alpha$:η^2-C≡C-*t*-Bu)(C$_6$F$_5$)(PPh$_2$H)]$_2$ (**1a**) (0.425 g, 0.338 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 45 min. The solution was evaporated to a small volume (ca. 2 mL), and addition of cold ethanol (3 mL) gave **2a** as a white solid (0.479 g, 87% yield). Complex **2b** (56% yield) was prepared in a similar way by using **1b** (0.35 g, 0.270 mmol) and 98.1 μL of PPh$_2$H (0.539 mmol) as starting materials, but in this case the solvent was evaporated and the final residue was treated with *n*-hexane.

2a. Anal. Calcd for $C_{36}F_5H_{31}P_2Pt$: C, 53.01; H, 3.83. Found: C, 52.73; H, 3.54. MS: *m*/*z* 815 ([M]$^+$, 44), 734 ([M − C≡C-*t*-Bu]$^+$, 82), 647 ([M − C$_6$F$_5$ − 1]$^+$, 33), 566 ([Pt(PPh$_2$)$_2$ + 1]$^+$, 100), 379 ([PtPPh$_2$ − 1]$^+$, 40). IR (ν_{max}/cm^{-1}): 2352 (w) (PH), (C≡C) not observed, 788 (s) (C$_6$F$_5$)$_{X-sens}$. ^{19}F NMR at 20 °C: δ −116.6 [dm, F$_o$, ^3J(Pt−F$_o$) = 274], −162.7 (t, F$_p$), −164.3 (m, F$_m$).^{13}C{^{1}H} NMR at 20 °C: δ 146.8 [dd, ^1J(C−F) ∼ 222, ^2J(C−F) ∼ 22, C$_6$F$_5$], 133.5 (dm, "*J*" ∼258, C$_6$F$_5$), 133.6 (s, C$_o$, PPh$_2$H), 130.4 (s, C$_p$, PPh$_2$H), 128.1 (s, C$_m$, PPh$_2$H), 122.0 [s, Cβ, Cα≡Cβ-*t*-Bu, ^2J(Pt−C) = 250], 81.2 [m, Cα, Cα≡Cβ-*t*-Bu, ^1J(Pt−C) ∼ 910], 31.5 [s, C(*C*H$_3$)$_3$], 28.9 [s, *C*Me$_3$, ^3J(Pt−C) = 19.1]. ^{31}P{^{1}H}NMR: δ −6.15, ^1J(Pt−P) = 2656.

2b. Anal. Calcd for $C_{38}F_5H_{27}P_2Pt$: C, 54.62; H, 3.26. Found: C, 54.21; H, 3.07. EI-MS (apci+): *m*/*z* 920 ([Pt(C$_6$F$_5$)(PPh$_2$H)$_3$]$^+$, 100), 836 ([M + 1]$^+$, 13), 735 ([M − C≡CPh]$^+$, 26). IR (ν_{max}/cm^{-1}): 2099 (w) (C≡C), 782 (w) (C$_6$F$_5$)$_{X-sens}$. ^{19}F NMR at 20 °C: δ −116.9 [dm, F$_o$, ^3J(Pt−F$_o$) = 274], −162.1 (t, F$_p$), −163.9 (m, F$_m$). The low stability of this complex prevented the acquisition of the ^{13}C NMR spectrum. ^{31}P{^{1}H}NMR: δ −6.53, ^1J(Pt−P) = 2621.

Preparation of *trans,cis*-[(C$_6$F$_5$)(PPh$_2$H)Pt(μ-κC$^\alpha$:η^2-C≡CR)(μ-PPh$_2$)RhCOD] (R = *t*-Bu, 3a; R = Ph, 3b). To a solution of *trans*-[Pt(C$_6$F$_5$)(C≡C-*t*-Bu)(PPh$_2$H)$_2$] (**2a**) (0.150 g, 0.184 mmol) in acetone (15 mL) was added a stoichiometric amount of [Rh(acac)COD] (0.057 g, 0.184 mmol). The resulting orange solution was stirred for 4 h and concentrated to small volume (2 mL) to give a microcrystalline orange solid, which was filtered off and washed with cold acetone (2 × 2 mL) (0.123 g, 65% yield).

Complex **3b** was prepared similarly as an orange solid by using the appropriate starting materials [**2b** (0.100 g, 0.120 mmol) and [Rh(acac)COD] (0.037 g, 0.12 mmol)], after 3 h of stirring, evaporation to small volume (ca. 2 mL), and treatment with *n*-hexane (10 mL) (0.078 g, 62% yield).

3a. Anal. Calcd for $C_{44}F_5H_{42}P_2PtRh$: C, 51.52; H, 4.13. Found: C, 51.26; H, 3.70. MS: *m*/*z* 1025 ([M]$^+$, 242), 917 ([M − COD]$^+$, 17), 813 ([M − Rh(COD) − 1]$^+$, 20), 590 ([Pt(PPh$_2$)Rh(COD) − 1]$^+$, 50), 512 ([Pt(PPh$_2$)PRh − 2]$^+$, 100), 436 ([Pt(PPh)PRh − 1]$^+$, 62). IR (ν_{max}/cm^{-1}): 2022 (w) (C≡C), 787 (s) (C$_6$F$_5$)$_{X-sens}$. ^{19}F NMR at −50 °C: δ −113.4, −116.2 [s, br, F$_o$, ^3J(Pt−F$_o$) = 343, 320], −163.3 (s, F$_p$), −164.6, −164.8 (overlapping of two F$_m$). At 20 °C: δ −115.2 [br, F$_o$, Pt satellites are observed but ^3J(Pt−F$_o$) cannot be calculated], −164.0 (t, F$_p$), −165.2 (m, F$_m$). At +50 °C: δ −115.3 [s, F$_o$, ^3J(Pt−F$_o$) = 362], −164.2 (t, F$_p$), −165.3 (m, F$_m$). ^{13}C{^{1}H} NMR at −50 °C: δ 146.4 [dd, ^1J(C−F) ∼ 210, ^2J(C−F) ∼ 20, C$_6$F$_5$], 137.4−130.5 (br, overlapping of C$_6$F$_5$ and Ph groups), 128.4 [d, *J*(C−P) = 9.9 Hz], 126.9 (s, br) (Ph), 119.0 [m, ^2J(Pt−Cβ) = 243, Cβ, Cα≡Cβ-*t*-Bu)], Cα is not observed, 94.1, 91.3, 71.2, 69.4 (br, =CH, COD), 37.3, 32.7 (CH$_2$, COD), 31.9 [s, br, C(*C*H$_3$)$_3$], 30.6 (s, *C*Me$_3$), 28.2, 26.1 (CH$_2$, COD).

3b. Anal. Calcd for $C_{46}F_5H_{38}P_2PtRh$: C, 52.83; H, 3.66. Found: C, 52.26; H, 3.66. MS: *m*/*z* 936 ([M − COD − 1]$^+$, 17), 813 ([M − Rh(COD) − 1]$^+$, 19), 512 ([Pt(PPh$_2$)PRh − 2]$^+$, 100), 436 ([Pt(PPh)PRh − 1]$^+$, 64). IR (ν_{max}/cm^{-1}): 2328 (w) (PH), 2020 (w) (C≡C), 782 (m) (C$_6$F$_5$)$_{X-sens}$. ^{19}F NMR at 20 °C: δ −114.8 [dm, F$_o$, ^3J(Pt−F$_o$) = 340], −163.7 (t, F$_p$), −165.1, (m, F$_m$). A similar spectrum is observed at −50 °C. Compound **3b** is not soluble enough for ^{13}C NMR studies.

Reactions of *trans*-[Pt(C$_6$F$_5$)(C≡CR)(PPh$_2$H)$_2$] and [Rh(acac)(CO)$_2$]. Formation of *trans,cis*-[(C$_6$F$_5$)(PPh$_2$H)Pt(μ-κC$^\alpha$:η^2-C≡C-*t*-Bu)(μ-PPh$_2$)Rh(CO)$_2$] (4a). [Rh(acac)(CO)$_2$] (0.046 g, 0.18 mmol) was added to a solution of *trans*-[Pt(C$_6$F$_5$)(C≡C-*t*-Bu)(PPh$_2$H)$_2$] (**2a**) (0.146 g, 0.179 mmol) in acetone (15 mL). The initial orange solution progressively turned dark brown. After 48 h of stirring at 20 °C, the resulting solution was evaporated to dryness, giving an oily brown residue, which was identified as **4a** by ^{31}P{^{1}H} NMR.

The reaction is slow, and we observed the presence of starting materials (by ^{31}P{^{1}H} NMR spectroscopy) until ∼48 h of reaction. Because of this long reaction period some decomposition also takes place.

The reaction between [Rh(acac)(CO)$_2$] (0.044 g, 0.17 mmol) and **2b** (0.142 g, 0.170 mmol) in acetone (25 mL) at 20 °C renders after 7 h of stirring a green solid (rhodium starting material), and the ^{31}P{^{1}H} NMR of the solution shows **2b** (traces) and considerable quantities of decomposition products. In thf, **2b** is detected in the solution even after 48 h of stirring, together with an unidentified mixture of products.

4a. It contains traces of impurity. MS: *m*/*z* 973 ([M]$^+$, 49), 947 ([M − CO + 2]$^+$, 52), 812 ([M − Rh(CO)$_2$ − 2]$^+$, 72), 737 ([M − Rh(CO)$_2$ − Ph + 1], 93), 512 ([Pt(PPh$_2$)PRh − 2]$^+$, 100), 436 ([Pt(PPh)PRh − 1]$^+$, 75). IR (ν_{max}/cm^{-1}): 2059 (s), 2000 (s, br) (C≡C, CO), 791 (m) (C$_6$F$_5$)$_{X-sens}$. ^{19}F NMR at 20 °C: δ −115.0 [dm, F$_o$, ^3J(Pt−F$_o$) = 343], −164.6 (t, F$_p$), −165.4 (m, F$_m$). The very low stability of this complex in solution prevented its characterization by ^{13}C NMR spectroscopy.

(25) Usón, R.; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* **1985**, *4*, 1912.
(26) (a) Varshavskii, Yu. S.; Cherkasova, T. G. *Russ J. Inorg. Chem.* **1967**, *12*, 899. (b) Bonatti, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156. (c) Robinson, S. R.; Shaw, B. L. *J. Chem. Soc.* **1965**, 4997.

Preparation of *cis,cis*-[(C≡CR)(PPh$_2$H)Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡CR)(*μ*-PPh$_2$)RhCOD] (R = *t*-Bu, 5a; R = Ph, 5b). To a yellow solution of *cis*-[Pt(C≡C-*t*-Bu)$_2$(PPh$_2$H)$_2$] (0.200 g, 0.274 mmol) in acetone (10 mL) was added [Rh(acac)COD] (0.085 g, 0.274 mmol) at −20 °C. The resulting brown solution was allowed to warm to 20 °C, and after 1 h of stirring, an orange solid started to precipitate. Stirring was continued for 4 h, and then the resulting solid was filtered off and washed with cold acetone (2 × 2 mL). This solid was identified as *cis,cis*-[(C≡C-*t*-Bu)(PPh$_2$H)Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡C-*t*-Bu)(*μ*-PPh$_2$)RhCOD] (**5a**) (0.196 g, 76% yield).

Complex **5b** was prepared similarly as a yellow solid by using the appropriate starting materials, *cis*-[Pt(C≡CPh)$_2$(PPh$_2$H)$_2$] (0.200 g, 0.260 mmol) and [Rh(acac)COD] (0.081 g, 0.26 mmol) (0.173 g, 68% yield).

5a. Anal. Calcd for $C_{44}H_{51}P_2PtRh$: C, 56.23; H, 5.47. Found: C, 55.87; H, 5.60. MS: *m*/*z* 858 ([M − C≡C-*t*-Bu]$^+$, 28), 831 ([M − COD]$^+$, 23), 591 ([Pt(PPh$_2$)Rh(COD)]$^+$, 32), 512 ([Pt(PPh$_2$)PRh − 2]$^+$, 100), 436 ([Pt(PPh)PRh − 1]$^+$, 68), 405 ([Pt(PPh)Rh − 1]$^+$, 29), 359 ([PtP$_2$Rh − 1]$^+$, 31). IR (ν_{max}/cm^{-1}): 2358 (w) (tentatively assigned to PH). ^{13}C{^{1}H} NMR at −50 °C: *δ* 135.0 (m), 134.8 (s, br), 134.4 (s, br) (Ph), 134.0 [d, C$_o$, *J*(C−P) = 10.1, PPh$_2$H], 130.2 (s, C$_p$, PPh$_2$H), 130.1 (s, Ph), 129.4 (s, Ph), 128.3 [d, C$_m$, *J*(C−P) = 10.3, PPh$_2$H], 128.1 (s, Ph), 127.4 [d, C$_m$, *J*(C−P) = 9.3, PPh$_2^-$], 122.4 [dd, C$_\beta$, C$_\alpha$≡C$_\beta$-*t*-Bu (b), ^3J(C−P$_{trans}$) = 31.0, ^3J(C−P$_{cis}$) = 9.1], 120.4 [d, C$_\beta$, C$_\alpha$≡C$_\beta$-*t*-Bu (t), ^3J(C−P$_{trans}$) = 24.9], 95.5 (s, br, =CH, COD, trans to P), 87.4 [dd, C$_\alpha$, C$_\alpha$≡C$_\beta$-*t*-Bu (t), ^2J(C−P$_{trans}$) = 104.2, ^2J(C−P$_{cis}$) = 16.5], 83.2 [dd, C$_\alpha$, C$_\alpha$≡C$_\beta$-*t*-Bu (b), ^2J(C−P$_{trans}$) = 142.1, ^2J(C−P$_{cis}$) = 36.4], 72.0 [d, *J*(C−Rh) = 13.1, =CH, COD, trans to C≡C-*t*-Bu], 32.8 [s, *C*Me$_3$ (b), CH$_2$, COD], 32.5, 32.0 [s, C(*C*H$_3$)$_3$ (b and t)], 29.4 (s, CH$_2$, COD), 29.1 [s, *C*Me$_3$ (t)].

5b. Anal. Calcd for $C_{48}H_{43}P_2PtRh$: C, 58.84; H, 4.42. Found: C, 59.30; H, 3.95. MS: *m*/*z* 871 ([M − COD]$^+$, 33), 770 ([M − COD − C≡CPh]$^+$, 12), 590 ([Pt(PPh$_2$)Rh(COD) − 1]$^+$, 37), 512 ([Pt(PPh$_2$)-PRh − 2]$^+$, 100), 436 ([Pt(PPh)PRh − 1]$^+$, 86), 404 ([Pt(PPh)Rh − 2]$^+$, 43), 359 ([PtP$_2$Rh − 1]$^+$, 40). IR (ν_{max}/cm^{-1}): 2108 (m) (C≡C). ^{13}C{^{1}H} NMR at −50 °C: *δ* 135.4 (m), 134.4 (d), 134.1 (s), 133.7 (s), 131.1 (s), 130.9 (s), 130.6 (s), 128.9 (s), 128.5 (d), 128.1 (s), 127.6 (d), 127.3 (s), 127.0 (s), 125.0 (s), (Ph), 113.4 [dd, C$_\beta$, C$_\alpha$≡C$_\beta$Ph (b), ^3J(C−P$_{trans}$) = 32.9, ^3J(C−P$_{cis}$) = 8.5], 111.7 [d, C$_\beta$, C$_\alpha$≡C$_\beta$Ph (t), ^3J(C−P$_{trans}$) = 26.7], 103.2 [dd, C$_\alpha$, C$_\alpha$≡C$_\beta$Ph (t), ^2J(C−P$_{trans}$) = 102.8, ^2J(C−P$_{cis}$) = 17.8], 100.3 (s, br, =CH, COD trans to P), 86.6 [dd, C$_\alpha$, C$_\alpha$≡C$_\beta$Ph (b), ^2J(C−P$_{trans}$) = 145.1, ^2J(C−P$_{cis}$) = 39.9], 73.3 [d, *J*(C−Rh) = 12.9, =CH, COD trans to C≡CPh], 32.4 (br, CH$_2$, COD), 28.5 (s, CH$_2$, COD).

Reactions of *cis*-[Pt(C≡CR)$_2$(PPh$_2$H)$_2$] (R = *t*-Bu; R = Ph) with [Rh(acac)(CO)$_2$]. Preparation of *cis,cis*-[(C≡C-*t*-Bu)(PPh$_2$H)Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡C-*t*-Bu)(*μ*-PPh$_2$)Rh(CO)$_2$] (6a). [Rh(acac)(CO)$_2$] (0.18 g, 0.69 mmol) was added to a stirred solution of *cis*-[Pt(C≡C-*t*-Bu)$_2$-(PPh$_2$H)$_2$] (0.50 g, 0.70 mmol) in acetone (20 mL) at −20 °C, and the mixture was stirred for 30 min and then allowed reach 20 °C. In a few minutes a yellow solid started to precipitate, and after 1 h of stirring the solid was filtered and washed with cold acetone (2 × 2 mL), 0.41 g (67% yield). The ^{31}P{^{1}H} NMR spectrum of this solid shows it to be the complex *cis,cis*-[(C≡C-*t*-Bu)(PPh$_2$H)Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡C-*t*-Bu)(*μ*-PPh$_2$)Rh(CO)$_2$] (**6a**) impurified with traces of the binuclear complex [Pt(C≡C-*t*-Bu)(*μ*-PPh$_2$)(PPh$_2$H)]$_2$.[12b]

The reaction of *cis*-[Pt(C≡CPh)$_2$(PPh$_2$H)$_2$] (0.100 g, 0.130 mmol) with [Rh(acac)(CO)$_2$] (0.035 g, 0.13 mmol) in acetone (10 mL) at −10 °C was monitored by ^{31}P{^{1}H} NMR spectroscopy. After 2 h, a dark-brown solution was observed, with ^{31}P NMR indicating the presence of considerable amounts of starting material *cis*-[Pt(C≡CPh)$_2$(PPh$_2$H)$_2$] plus weak signals at *δ* −5.08 (d, *J* = 14.5) and −11.83 (d, *J* = 21.4). Similar results were observed when the reaction was carried out in a 1:2 ratio (Pt:Rh) for 40 min at 20 °C.

6a. Anal. Calcd for $C_{38}H_{39}O_2P_2PtRh$: C, 51.42; H, 4.43. Found: C, 50.91; H, 4.64. MS: *m*/*z* 1294 ([Pt(C≡C-*t*-Bu)(*μ*-PPh$_2$)(PPh$_2$H)]$_2^+$ = A$^+$, 56), 1213 ([A − C≡C-*t*-Bu]$^+$, 100), 1108 ([A − PPh$_2$H]$^+$, 22), 1026 ([A − C≡C-*t*-Bu − PPh$_2$H − 1]$^+$, 35), 946 ([Pt$_2$(PPh$_2$)$_2$(PPh$_2$H)]$^+$, 57), 887 ([M]$^+$, 18), 871 ([M − O]$^+$, 89), 689 ([Rh(*μ*-PPh$_2$)(CO)$_2$]$_2^+$= B$^+$ + 1, 28), 635 ([B − 2CO + 3]$^+$, 63), 605 ([B − 3CO + 1]$^+$, 41), 512 ([Pt(PPh$_2$)PRh − 2]$^+$, 68), 436 ([Pt(PPh)PRh − 1]$^+$, 68). IR (ν_{max}/cm^{-1}): 2340 (m) (PH) [C≡C: not assigned because of overlap with *ν*(CO)], 2066 (vs), 2002 (vs) (CO) with additional shoulders at 2035, 2020, and 1956, some of them probably also due to *ν*(C≡C). ^{13}C{^{1}H} NMR at −50 °C: *δ* 186.1 [dd, C≡O trans to P, ^1J(C−Rh) = 58.8, ^2J(C−P) = 92.6], 185.0 [dd, C≡O cis to P, ^1J(C−Rh) = 78.9, ^2J(C−P) = 10.8], 134.8 [d, C$_o$, *J*(C−P) = 11.1, PPh$_2^-$], 134.0 [d, C$_o$, *J*(C−P) = 10.5, PPh$_2$H], 130.5 (s, C$_p$, PPh$_2$H), 129.6 [C$_i$, ^2J(Pt−C) = 47], 129.0 (s, C$_p$, PPh$_2^-$), 128.3 [d, C$_m$, *J*(C−P) = 10.6, PPh$_2$H], 127.7 [d, C$_m$, *J*(C−P) = 10.5, PPh$_2^-$], 121.5 [dm, C$_\beta$, C$_\alpha$≡C$_\beta$-*t*-Bu (b), "*J*(C−P)" = 36.8], 120.4 ["d", C$_\beta$, C$_\alpha$≡C$_\beta$-*t*-Bu (t), ^3J(C−P$_{trans}$) = 26.5], 84.6 [dd, C$_\alpha$, C$_\alpha$≡C$_\beta$-*t*-Bu (t), ^2J(C−P$_{trans}$) = 110.7, ^2J(C−P$_{cis}$) = 18.0], 73.6 [dd, C$_\alpha$, C$_\alpha$≡C$_\beta$-*t*-Bu (b), ^2J(C−P$_{trans}$) = 139.4, ^2J(C−P$_{cis}$) = 28.9], 32.3, 31.8 [s, C(*C*H$_3$)$_3$ (b and t)], 31.6, 29.0 [s, *C*Me$_3$ (b and t)].

Preparation of [{(PPh$_2$O)$_2$H}Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡CR)(*μ*-*κP*,*κO*-PPh$_2$O)-RhCOD] (R = *t*-Bu, 7a; R = Ph, 7b). A suspension of [Pt(C≡C-*t*-Bu){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (0.150 g, 0.17 mmol) in acetone (20 mL) was cooled to −40 °C and treated with [Rh(acac)COD] (0.053 g, 0.17 mmol). The mixture was stirred for 3 h while being warmed to 20 °C, and then the resulting cloudy pale-yellow solution was filtered through Celite. Partial evaporation of the solvent and addition of *n*-hexane (5 mL) gave **7a** as a yellow-orange solid (0.109 g, 59% yield).

Complex **7b** was obtained as a yellow solid in a similar way by reaction of the appropriate starting materials [Pt(C≡CPh){(PPh$_2$O)$_2$H}-(PPh$_2$OH)] (0.150 g, 0.166 mmol) and [Rh(acac)COD] (0.0516 g, 0.166 mmol) in thf (20 mL) for 5 h from −25 to 20 °C (0.135 g, 73% yield).

7a. Anal. Calcd for $C_{50}H_{52}O_3P_3PtRh$: C, 55.00; H, 4.80. Found: C, 54.68; H, 4.36. MS: *m*/*z* 1091 ([M]$^+$, 40), 982 ([M − COD − 1]$^+$, 100), 882 ([Pt(C≡C-*t*-Bu){(PPh$_2$O)$_2$H}(PPh$_2$OH) + 1]$^+$, 33), 599 ([Pt-{(PPh$_2$O)$_2$H} + 1]$^+$, 20). IR (ν_{max}/cm^{-1}): 1029 (sh), 1011 (m), 994 (m), 979 (s) (PO).^{13}C{^{1}H} NMR at −50 °C: *δ* 142.2 [dd, $^{1,3}J$(C−P) = 48.6; 12.6], 140.2 [dd, $^{1,3}J$(C−P) = 50.6; 15.2], 139.4 [dd, $^{1,3}J$(C−P) = 46.6, 12.9], 138.1 [dd, $^{1,3}J$(C−P) = 68.8, 17.4], 136.3 [dd, $^{1,3}J$(C−P) = 46.9, 15.9] (C$_i$, PPh$_2$O$^-$, {PPh$_2$O}H), 133.9 [d, C$_o$, *J*(C−P) = 13.1], 132.8 [d, C$_o$, *J*(C−P) = 11.2], 131.1 [d, C$_o$, *J*(C−P) = 8.3], 130.8 (m), 130.3 (s, C$_p$), 129.6 (s, C$_p$), 129.3 [d, C$_m$, *J*(C−P) = 10.2], 128.8 (s, C$_p$), 127.9 [d, *J*(C−P) = 11.2, C$_m$], 127.6 (m, C$_m$), 127.1 [d, C$_m$, *J*(C−P) = 9.3], 126.7 [d, C$_m$, *J*(C−P) = 8.5] (PPh$_2$OH and PPh$_2$O$^-$), 113.4 [dm, C$_\beta$, C$_\alpha$≡C$_\beta$-*t*-Bu, ^3J(C−P) = 28.1], 89.9 [d, *J*(C−Rh) = 14.2, =CH, COD], 86.9 [dm, C$_\alpha$, C$_\alpha$≡C$_\beta$-*t*-Bu, ^2J(C−P) = 114.1], 80.6 [d, *J*(C−Rh) = 11.5], 75.0 [d, *J*(C−Rh) = 10.9], 69.1 [d, *J*(C−Rh) = 11.6] (=CH, COD), 34.3, 32.7, 28.8, 27.3 (s, CH$_2$, COD), 30.7 [s, C(*C*H$_3$)$_3$], 30.5 (s, *C*Me$_3$).

7b. Anal. Calcd for $C_{52}H_{48}O_3P_3PtRh$: C, 56.17; H, 4.35. Found: C, 56.05; H, 4.58. MS: *m*/*z* 1112 ([M + 1]$^+$, 33), 1003 ([M − COD]$^+$, 100), 902 ([M − COD − C≡CPh]$^+$, 35), 599 ([Pt{(PPh$_2$O)$_2$H} + 1]$^+$, 18). IR (ν_{max}/cm^{-1}): 2019 (w) (C≡C), 1028 (sh), 1010 (m), 996 (m), 974 (s) (PO). Its low solubility prevented characterization by ^{13}C NMR spectroscopy.

Reactions of [Pt(C≡CR){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (R = *t*-Bu; R = Ph) with [Rh(acac)(CO)$_2$]. Formation of 8a and 8b. A cooled (−20 °C) suspension of [Pt(C≡C-*t*-Bu){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (0.125 g, 0.142 mmol) in acetone was treated with [Rh(acac)(CO)$_2$] (0.0402 g, 0.156 mmol) and stirred for 2 h while the mixture warmed to 20 °C. The resulting yellow solution was filtered through Celite, and the solvent was removed in a vacuum to give an oily residue very soluble in common precipitating solvents, which was characterized spectroscopically (see Tables 1 and 2) as [{(PPh$_2$O)$_2$H}Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡C-*t*-Bu)-(*μ*-*κP*,*κO*-PPh$_2$O)Rh(CO)$_2$] (**8a**). Its very low stability in solution prevented its characterization by ^{13}C NMR spectroscopy.

The analogous reaction with the phenyl starting material (0.100 g, 0.111 mmol of [Pt(C≡CPh){(PPh$_2$O)$_2$H}(PPh$_2$OH)]) and 0.034 g, 0.13 mmol of [Rh(acac)(CO)$_2$] was carried out in thf (25 mL). The initial suspension dissolved slowly, and after 1 h, the resulting yellow solution was filtered through Celite and the solvent removed in a vacuum to give [{(PPh$_2$O)$_2$H}Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡CPh)(*μ*-*κP*,*κO*-PPh$_2$O)Rh(CO)$_2$] (**8b**) as an oily residue, which was characterized spectroscopically (Tables 1 and 2).

Preparation of [{(PPh$_2$O)$_2$H}Pt(*μ*-*κC*$^\alpha$:*η*^{2}-C≡CR)(*μ*-*κP*,*κO*-PPh$_2$O)-IrCOD] (R = *t*-Bu, 9a; R = Ph, 9b). Complexes **9a** and **9b** were prepared as orange solids in a similar way to **7a** and **7b**, respectively, starting from [Pt(C≡C-*t*-Bu){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (0.150 g, 0.170

mmol) and [Ir(acac)COD] (0.068 g, 0.17 mmol) for **9a** (0.143 g, 71% yield) and [Pt(C≡CPh){$(PPh_2O)_2H$}(PPh_2OH)] (0.125 g, 0.139 mmol) and [Ir(acac)COD] (0.055 g, 0.14 mmol) for **9b** (0.122 g, 73% yield). Longer reaction times (7 h, **9a**, and 24 h, **9b**) were required.

9a. Anal. Calcd for $C_{50}H_{52}O_3P_3PtIr$: C, 50.84; H, 4.44. Found: C, 50.75; H, 4.36. MS: *m*/*z* 1181 ($[M + 1]^+$, 10), 1073 ($[M - COD - 1]^+$, 23), 882 ($[Pt(C{\equiv}C\text{-}t\text{-}Bu)\{(PPh_2O)_2H\}(PPh_2OH) + 1]^+$, 100), 599 ($[Pt\{(PPh_2O)_2H\} + 1]^+$, 42). IR ($\nu_{max}$/$cm^{-1}$): 1028 (sh), 1012 (s), 996 (m), 962 (s) (PO).

9b. Anal. Calcd for $C_{52}H_{48}O_3P_3PtIr$: C, 52.00; H, 4.03. Found: C, 52.51; H, 4.79. MS: *m*/*z* 1201 ($[M + 1]^+$, 5), 1093 ($[M - COD + 1]^+$, 11), 399 ($[Pt(PPh_2OH) + 2]^+$, 100). IR (ν_{max}/cm^{-1}): 2339 (w) (PH), 2019 (w) (C≡C), 1027 (sh), 1014 (m), 997 (m), 965 (m) (PO).

The very low solubility of **9a** and **9b** prevented their characterization by ^{13}C NMR.

X-ray Crystallography of 6a. Crystals of **6a** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a chloroform solution of **6a** at −30 °C. Important crystal data and data collection parameters are listed in Table 4. A crystal of **6a** was mounted at the end of a quartz fiber and held in place with a fluorinated oil. All diffraction measurements were made at 150(1) K on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα X-radiation. Unit cell dimensions were determined from 25 centered reflections in the range $22.3° < 2\theta < 31.5°$. Diffracted intensities were measured in a hemisphere of reciprocal space for $4.0° < 2\theta < 50.0°$ by ω scans. Three check reflections remeasured after every 3 h showed no decay of the crystal over the period of data collection. An absorption correction was applied on the basis of 370 azimuthal scan data (maximum and minimum transmission coefficients were 0.908 and 0.677). The structure was solved by Patterson methods. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. The hydrogen atoms of the complex were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their parent carbon atoms (1.5 times for the methyl hydrogen atoms). Full-matrix least-squares refinement of this model against F^2 converged to final residual indices given in Table 4. A final difference electron density map showed no peaks above 1 e $Å^{-3}$ (largest difference peak 0.62; largest difference hole −0.66). Least-squares calculations were carried out using the program SHELXL-93.[27]

Table 4. Crystallographic Data for *cis*,*cis*-[(C≡C-*t*-Bu)(PPh_2H)-Pt(μ-κC^{α}:η^2-C≡C-*t*-Bu)(μ-PPh_2)Rh($CO)_2$] (**6a**)

empirical formula	$C_{38}H_{39}O_2P_2PtRh$
fw	887.63
temp (K)	150(1)
wavelength (Å)	0.710 73
space group	$P\bar{1}$
unit cell dimens	
a (Å)	11.427(2)
b (Å)	12.882(2)
c (Å)	14.692(2)
α (deg)	99.098(14)
β (deg)	108.339(12)
γ (deg)	113.11(2)
vol ($Å^3$)	1787.2(4)
Z	2
ρ_{calc} (Mg/m^3)	1.65
abs coeff (mm^{-1})	4.49
final *R* indices[a] [$I > 2\sigma(I)$]	R1 = 0.0320, wR2 = 0.0661
R indices[a] (all data)	R1 = 0.0458, wR2 = 0.0708

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Acknowledgment. We thank the Dirección General de Enseñanza Superior (Spain) (Projects PB95-0003-C02-01-02 and PB95-0792) and the University of La Rioja (Project API-99/B17 and a grant for J.G.) for financial support.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for complex **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9900049

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