676 *Organometallics* 1987, *6*, 676–678

Communications

Synthesis and Characterization of a Copper(I) Triflate Complex of 1,2:5,6:9,10-Tribenzocyclododeca-1,5,9-triene-3,7,11-triyne

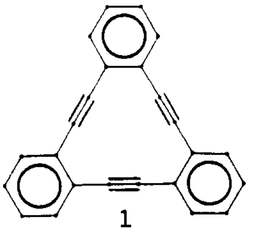
Joseph D. Ferrara, Claire Tessier-Youngs, and Wiley J. Youngs*

Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

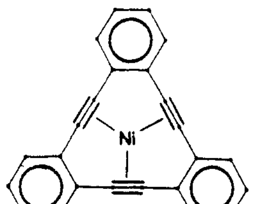
Received January 27, 1986

Summary: A copper(I) triflate complex of 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne (**1**) has been synthesized and characterized by X-ray crystallography, NMR and IR spectroscopies, and elemental analysis. The copper(I) ion of the complex **3** is chelated by the three alkynes of **1** and semicoordinated by an oxygen of the triflate anion. Complex **3** disproportionates to Cu(0) and Cu(II) in THF solution.

As part of our continuing studies of transition-metal complexes of cyclynes and their possible application as conducting materials,[1] we have investigated the interaction of 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne[2] (1) with [μ-[(1,2-η:3,4-η)-C_6H_6]]bis(trifluoromethanesulfonato-*O*)dicopper[3] (copper benzene triflate). Our previous[1] work in this field produced a complex (2) in which a nickel atom was chelated by the three alkynes of the cyclyne 1. We now wish to report the synthesis of a Cu(I) triflate complex of 1, $Cu(C_{24}H_{12})(OSO_2CF_3)$ (3), in which the copper ion is formally isoelectronic to the nickel atom of 2. The related complex $Cu(C_{24}H_{12})(OSO_2CF_3)\cdot(C_{24}H_{12})$ (4) has been crystallographically characterized.



1



2

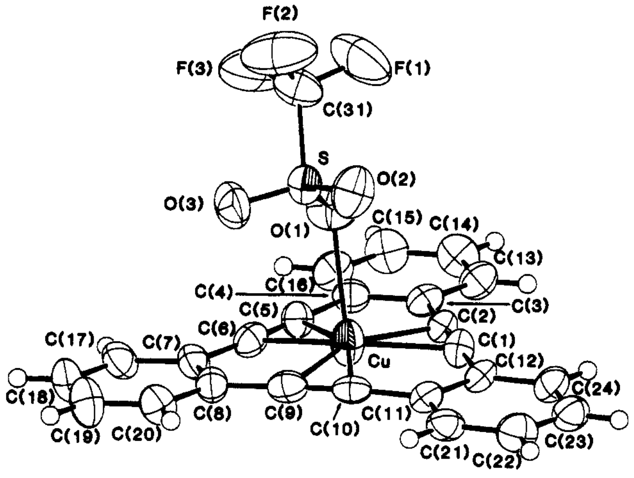


Figure 1. ORTEP labeling diagram for $Cu(C_{24}H_{12})(O_2SOCF_3)$. The thermal ellipsoids are drawn at the 50% probability level except for the hydrogen atoms which are drawn arbitrarily small for clarity.

All manipulations were done by using inert-atmosphere techniques.[4] Complex 3 was obtained by mixing saturated benzene solutions of $Cu_2(C_6H_6)(OSO_2CF_3)_2$[3] ($7.50 \times 10^{-2}$ g, 1.49×10^{-4} mol) and 1 (8.96×10^{-2} g, 2.98×10^{-4} mol). Complex 3 precipitates as a pale yellow air-sensitive powder. Elemental analysis of the powder is consistent with the formula $Cu(C_{24}H_{12})(SO_3CF_3)$.[5] The infrared spectrum of 3 shows a band at 2085 cm^{-1} assigned to the C≡C stretch.[6] The corresponding bands in the free ligand 1 and in the complex 2 occur at 2208 and 1955 cm^{-1}, respectively.[1,2a] The ^{1}H NMR spectrum of a freshly made THF-d_8 solution of 3 shows the symmetric ortho substitution pattern common to 1 and 2 with a small downfield shift from the spectrum of 1.[7] THF solutions of 3 change from pale yellow to green on standing for several days and become more viscous. Copper metal precipitates during this process. The green color is due to the formation of THF solvated $Cu(SO_3CF_3)_2$ as confirmed by comparison of the EPR spectrum of an authentic sample with that of the green solution.[8,9] An unidentified radical species is also observed in the EPR spectrum of the green solution.[8] A green pasty solid, presumably impure polytetrahydrofuran,[10] is isolated when the THF is removed. It has been

---

[1] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6719–6721.

[2] (a) Staab, H. A.; Graf, F. *Tetrahedron Lett.* **1966**, 751–757. (b) Campbell, I. D.; Eglington, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87–89.

[3] (a) Purchased from Strem Chemical and used without further purification. (b) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.

[4] Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; R. E. Krieger Publishing Co.: Malabar, FL, 1982.

[5] Schwarzkopf Microanalytical Laboratory, Analyzed for Cu, F, C, H. Found: Cu, 12.49; F, 11.95; C, 56.18; H, 2.50. Mikroanalytisches Labor Pascher, Analyzed for Cu, F, C, H. Calcd: Cu, 12.39; F, 11.11; C, 58.54; H, 2.36. Found: Cu, 12.8; F, 11.6; C, 56.16; H, 2.38. Both commercial analyses for carbon do not appear to analyze for carbon bound to fluorine. The calculated percentage for carbon not bound to fluorine is 56.19%.

[6] IR data (ν (cm^{-1}), intensity): 3070 w, 2085 w, 1584 w, 1476 m, 1441 w, 1377 w, 1291 s, 1243 s, 1218 s, 1155 s, 1026 s, 962 w, 766 s, 634 s, 604 m, 571 m, 517 m, 480 m. The spectra of a Nujol mull and a KBr pellet were recorded on a Mattson Cygnus 25 FT-IR with a resolution of 4 cm^{-1}.

[7] The ^{1}H NMR spectrum of 3 shows two multiplets (AA′BB′spin system) centered at δ 7.49 and 7.26. The ^{1}H NMR spectrum of 1 shows two multiplets (AA′BB′) centered at δ 7.33 and 7.22. All data were recorded on a Varian XL-200 at room temperature in THF-d_8, internal secondary reference (δ 3.58, 1.73). (For a discussion of A_2B_2 spin systems see: Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1969.)

[8] For the Cu(II) species in the green solution (THF-d_8): ambient temperature, $g_{iso} = 2.196$; 93 K, $g_{\perp} = 2.100$; $g_{\parallel} = 2.432$, $a_{\parallel} = 1.27 \times 10^{-3}$ cm^{-1}. For the radical species: ambient temperature, $g_{iso} = 1.984$. For $Cu(SO_3CF_3)_2$ in THF: ambient temperature, $g_{iso} = 2.206$; 93 K, $g_{\perp} = 2.086$, $g_{\parallel} = 2.406$, $a_{\parallel} = 1.28 \times 10^{-3}$ cm^{-1}. All data were recorded on a Varian E-10 spectrometer with DPPH as an external reference.

[9] (a) Woodhouse, M. E.; Lewis, F. D.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5586–5594. (b) Dreissen, W. L.; den Heijer, M. *Inorg. Chim. Acta* **1979**, *33*, 261–264.

[10] The ^{1}H NMR spectra of THF-d_8 solutions of 3 show the degradation of the signal from residual THF and new broad signals at δ 3.29 (t, *J* = 20 Hz) and 1.38 (q, *J* = 22 Hz).

0276-7333/87/2306-0676$01.50/0

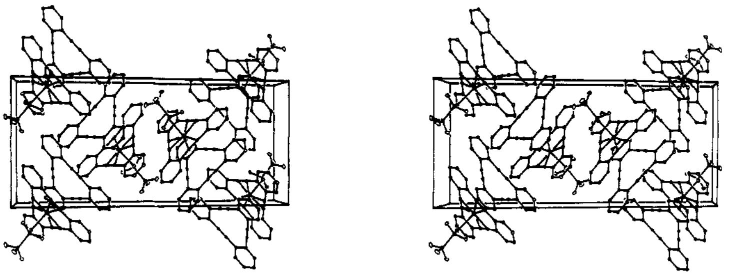


Figure 2. ORTEP packing diagram stereoview of $Cu(C_{24}H_{12})(O_2SOCF_3)\cdot(C_{24}H_{12})$. The ellipsoids are drawn at the 5% probability level, and the hydrogens are omitted for clarity. The *a* axis points to the viewer, and the *c* axis points to the right.

established that THF solutions of $Cu_2(C_6H_6)(OSO_2CF_3)_2$ undergo a disproportionation to Cu(0) and $Cu(SO_3CF_3)_2$ with concomitant polymerization of the THF.[9a] Our results indicate that a similar process occurs in THF solutions of **3**.

Slow removal of the THF from the green solution affords yellow, moderately air-stable crystals of complex **4**. Elemental analysis of these crystals for C and H is consistent with the formula $Cu(C_{24}H_{12})(OSO_2CF_3)\cdot(C_{24}H_{12})$.[11] The infrared spectra of **3** and **4** are identical except for the additional bands due to the cocrystallized ligand **1** in the spectrum of **4**. The cocrystallized ligand **1** is further evidence for the disproportionation of **3** because free ligand must be generated as Cu(0) forms. Direct reaction of **1** and $Cu_2(C_6H_6)(OSO_2CF_3)_2$ in a 4:1 molar ratio in diethyl ether or benzene results in the quantitative precipitation of complex **3**, not **4**. Dissolution of the products of the former reaction in THF, followed by addition of hexane to induce rapid crystallization, yields complex **4**.

A crystal of **4** of hexagonal habit was found to be suitable for X-ray diffraction studies and intensity data were collected on a Syntex $P2_1$ diffractometer.[12] The structure was solved by direct methods and refined to convergence ($R(F)$ = 0.048).[13] Structure solution showed that the asymmetric unit of **4** (space group $P2_1/c$) contained two molecules, one of complex **3** and one of the uncomplexed ligand **1**. The crystal structure of the free ligand **1** has been previously reported, and there are no significant differences between the two crystallographically determined molecular structures.[14] The overall geometry of **3** can be described as trigonal pyramidal with the Cu(I) ion coordinated by the three alkynes of the cyclyne and an oxygen atom of the triflate. In the complex and the free ligand, all 24 carbon atoms are nearly planar. The copper atom in **3** is 0.18 Å above the least-squares plane defined by the six acetylenic carbon atoms (root-mean-square deviation = 0.017 Å). The distortion of the cyclyne ligand induced by metal coordination is less in the copper complex **3** than in the nickel complex **2**. The C≡C bond length in **3** is 1.222 (10) Å while in **2** it is 1.240 (10) Å compared with 1.182 (10) Å for the free ligand **1**. The C≡C—C angle in **3** is 177.8 (6)° while in **2** it is 173.8 (9)° and in **1** it is 178.9 (6)°. A correlation between the C≡C—R angle and the C≡C bond length for 70 π-bound alkyne metal complexes has recently appeared.[15] Compared to these complexes, **2** and **3** show the least distortion from linearity for the C≡C—C fragment. The mean Cu–C bond length in **3** is 2.060 (4) Å, while in **2** the mean Ni–C bond length is 1.958 (5) Å. The semicoordinating nature of the triflate anion of **3** prevents the stacking of the planar $Cu(I)(C_{24}H_{12})$ cations (Figure 2). Extended slip stacking is observed in the structure of the neutral nickel complex **2**.[1] The copper cyclyne to free cyclyne interplanar distance is 3.52 (8) Å with the benzo groups eclipsed. The dihedral angle between these planes is approximately 2°.

The semicoordinating nature of the triflate ion deserves special comment.[16] The distance between the Cu(I) and the oxygen of the triflate in **3** (2.549 (5) Å) is considerably longer than typical Cu(I)–O bond lengths (1.83–2.23 Å) and is longer than the Cu(I)–O distance between $Cu(CO)L^+$ (L = di-2-pyridylamine) and a semicoordinating perchlorate anion (2.429 Å).[17,18] Other transition-metal complexes with monodentate $CF_3SO_3^-$ have been crystallographically characterized, and the metal to triflate oxygen distances are shorter (2.00–2.49 Å; metals = Fe, Au, Pd, Ti, and Ag).[19,24] Semicoordination of the anions BF_4^- and $B(C_6H_5)_4^-$ to Cu(I) has been previously reported.[20] In contrast to the semicoordination of the $CF_3SO_3^-$ in **3**, the triflate anions of the complexes $Cu_2(C_6H_6)(SO_3CF_3)_2$ and $Cu(C_6H_{10})(SO_3CF_3)$ are di- or tribridging as part of polymeric structures with Cu(I)–O bond lengths in the range 2.05–2.59 Å.[21] The infrared spectra of KBr pellets of **3** or **4** show a weak band at ~1380 cm^{-1} which is consistent with monodentate bound triflate.[19] In addition, the number of bands in the SO_3–CF_3 stretch range (~1000–1385 cm^{-1}) suggest that the symmetry of the triflate ion is lower than the C_{3v} symmetry expected for the uncoordinated anion.[19,21,22] As in other structures with semicoordinated triflates, the bonding within the $CF_3SO_3^-$ closely resembles that of the free ion.[19,23]

---

[11] Schwarzkopf Microanalytical Laboratory, Analyzed for C and H. Calcd: C, 72.36; H, 2.97. Found: C, 68.80; H, 2.99. The calculated percentage for carbon not bound to fluorine is 70.88%. See comment in ref 5.

[12] Crystallographic data: space group $P2_1/c$, a = 11.119 (2) Å, b = 12.256 (2) Å, c = 28.191 (5) Å, β = 105.39 (1)°; ρ_{calcd} = 1.4582 (4) g cm^{-3}, ρ_{obsd} = 1.49 (1) g cm^{-3}; Z = 4; fw = 813.35. The intensity data were collected from $3.0 \le 2\theta \le 50.0°$. Refinement to convergence on the 2492 unique reflections, $I \ge 3\sigma(I)$, resulted in final anisotropic R = 0.048 and R_w = 0.049.

[13] The UCLA Crystallographic Computing Package, Jan 5, 1982.

[14] Irngartinger, H.; Leiserowitz, L.; Schmidt, G. M. J. *Chem. Ber.* **1970**, *103*, 1119–1131.

[15] Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612–1619.

[16] Semicoordination has been defined and reviewed in: Rosenthal, M. R., *J. Chem. Educ.* **1973**, *50*, 331.

[17] (a) Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1252–1253 and references cited therein. (b) Rodesiler, P. F.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1974**, 599–600 and references cited therein.

[18] Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813–2819. We thank a reviewer for bringing this paper and those in ref 20 to our attention.

[19] Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17–33 and references cited therein.

[20] (a) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191–1197. (b) Gaughan, A. P., Jr.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657–1667.

[21] (a) Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12. (b) Timmermans, P. J. J. A.; Mackor, A.; Spek, A. L.; Kojić-Prodić B. *J. Organomet. Chem.* **1984**, *276*, 287–295.

[22] (a) Dedert, P. L.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 3506–3517. (b) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969–977 and references cited therein.

[23] Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355–3358 and references cited therein.

We are currently investigating the effects of stoichiometry and conditions on the reaction of 1 with $Cu_2(C_6H_6)(SO_3CF_3)_2$. A multinuclear complex of 1 has been isolated with excess $Cu_2(C_6H_6)(SO_3CF_3)_2$. The synthesis of Cu(I) complexes of the cyclyne 1 with other anions that may promote stacking and related silver chemistry are being explored.

Acknowledgment. We thank Professors M. E. Kenney, R. G. Salomon, and F. L. Urbach for helpful discussions. J.D.F. thanks the BFGoodrich Co. for financial support through the BFGoodrich Fellowship at CWRU. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and an Olin Corporation Charitable Trust Grant of the Research Corp. for partial support of this work.

Supplementary Material Available: Tables of data collection and structure solution details, bonds lengths and angles, and atomic positional and thermal parameters (10 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

---

[24] Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* 1985, *107*, 1979–1985.

Synthesis and Characterization of New Rhodium and Iridium Complexes Containing the Heterodifunctional Ligand (Diphenylphosphino)cyclopentadienyl

XiaoDong He,[1a] André Maisonnat,[1b] Françoise Dahan,[1b] and René Poilblanc*[1b]

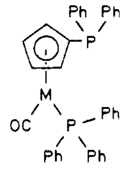
Laboratoire de Chimie de Coordination du CNRS
Unité No. 8241
liée par convention à l'Université Paul Sabatier
31077 Toulouse Cedex, France

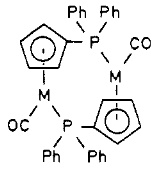
Received July 22, 1986

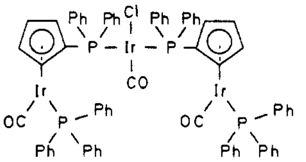
Summary: The new complexes $(\eta^5\text{-}C_5H_4)PPh_2M(CO)(PPh_3)$ (**1a**, M = Rh; **1b**, M = Ir), $[(\eta^5\text{-}C_5H_4)PPh_2]_2M_2(CO)_2$ (**2a**, M = Rh; **2b**, M = Ir), and $IrCl(CO)Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)_2$ (**3b**) have been prepared and characterized. In the mononuclear complexes **1a** and **1b**, the heterodifunctional ligand possesses a free phosphine group that may attach to a second metal center as illustrated by the conversion of **1a** into the dinuclear complex **2a**. Complexes **2a** and **2b** have dinuclear symmetrical structures where the metallic centers are linked by two bridging (diphenylphosphino)cyclopentadienyl ligands in a "head-to-tail" configuration.

The heterodifunctional ligands containing a cyclopentadienide ring, directly linked to a phosphine group as in the (diphenylphosphino)cyclopentadienide anion (dppc)[2] or by a molecular chain as in (dimethyl((diphenylphosphino)methyl)silyl)cyclopentadienide[3] and ((diphenylphosphino)ethyl)cyclopentadienide[4] anions, have received significant attention in recent years because of their potential ability to join two metallic centers.[3,5–8]

Following our investigations on the synthesis and properties of new polymetallic complexes,[5,9] we report here our preliminary results on the interaction of the ligand $Ph_2P(C_5H_4)Li$ with $[RhCl(CO)(PPh_3)]_2$ and *trans*-$IrCl(CO)(PPh_3)_2$ to form new monometallic (**1a** and **1b**), dimetallic (**2a** and **2b**), and trimetallic (**3b**) species.


1a, M = Rh
1b, M = Ir


2a, M = Rh
2b, M = Ir


3

Addition of lithium (diphenylphosphino)cyclopentadienide to half an equimolar amount of the chloro-bridged dirhodium complex $Rh_2Cl_2(CO)_2(PPh_3)_2$ in toluene at 0 °C leads readily to the formation of a yellow precipitate of the dimetallic species **2a** and an orange solution containing the monometallic species **1a** together with free triphenylphosphine (eq 1).

$$\tfrac{1}{2}[RhCl(CO)(PPh_3)]_2 \xrightarrow[0\ ^\circ C,\ \text{toluene}\ -\text{LiCl}]{Li(C_5H_4)PPh_2} \underset{70\%}{\mathbf{1a}} + \underset{30\%}{\mathbf{2a}} + 2PPh_3 \qquad (1)$$

Complexes **1a** and **2a** were fully characterized by mass spectra and IR spectra in the ν(CO) region as well as ^{31}P and ^1H NMR spectra.[10] The $^{31}P\{^1H\}$ spectrum of **1a** in CD_2Cl_2 exhibits two signals of equal intensities: a doublet centered at +52.28 ppm with a doublet spacing of 198 Hz corresponding to a triphenylphosphine ligand bonded to an 18-electron rhodium(I) center and a singlet at −21.20 ppm indicative of a noncoordinated tertiary phosphine group. The $^{31}P\{^1H\}$ NMR spectrum of **2a**, exhibiting a typical pattern of an AA′XX′ spin system (δ 41.08 ($J_{P\text{-}Rh}$ = 200 Hz)), points out a symmetrical structure in which the phosphorus atom of each of both difunctional ligands

---

[1] (a) On leave from the Chengdu Institute of Organic Chemistry, Academia Sinica, Chengdu, China. (b) Full postal address: Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France.

[2] Mathey, F.; Lampin, J. P. *Tetrahedron* 1975, *31*, 2685–2690.

[3] (a) Shore, N. E. *J. Am. Chem. Soc.* 1979, *101*, 7410–7412. (b) Shore, N. E.; Benner, L. S.; La Belle, B. *Inorg. Chem.* 1981, *20*, 3200–3208.

[4] Charrier, C; Mathey, F. *J. Organomet. Chem.* 1979, *170*, C41–C43.

[5] Moïse, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* 1984, *231*, C43–C48.

[6] (a) Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A.; L. *Organometallics* 1982, *1*, 1591–1596. (b) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* 1983, *105*, 7574–7580. (c) Casey, C. P.; Nieff, F. *Organometallics* 1985, *4*, 1218–1220.

[7] Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* 1983, *105*, 3882–3886.

[8] Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* 1986, *5*, 888–894.

[9] (a) El Amane, M.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* 1985, *4*, 773–780. (b) Delavaux, B.; Chaudret, B.; Taylor, N. J.; Arabi, S.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* 1985, 805–807. (c) Maisonnat, A.; Poilblanc, R. *C. R. Acad. Sci., Ser. 2* 1984, 69–71.

[10] For **1a**: electron-impact MS (70 eV), *m/e* 610 (M^+) plus fragment ions from which one corresponds to the loss of one CO group; IR (ν(CO), in hexane) 1956 cm^{-1}. For **2a**: electron-impact MS, *m/e* 760 plus fragment ions corresponding to successive loss of two CO groups; IR (ν(CO), CH_2Cl_2) 1946 cm^{-1}. Anal. Calcd for $C_{36}H_{28}O_2P_2Rh_2$: C, 56.85; H, 3.71. Found: C, 57.68; H, 4.07.