= 106.2, H-1), 1.16 (brs, $J_{Pt,H}$ = 80.5, H-2), 0.76 (brd, $J_{H,H}$ = 8, $J_{Pt,H}$ = 113.2, H-1); ^{195}Pt NMR ($CDCl_3$) 1090 ppm. ^{13}C NMR ($CDCl_3$): see Table II.

Formation of 12a. Cuprous chloride (11.5 g, 116 mmol) and 7.6 g (116 mmol) of Zn dust were placed in a two-necked round-bottom flask containing 150 mL of dry diethyl ether. The mixture was charged with nitrogen and refluxed for 0.5 h with stirring. After 30 min 4.7 mL (58 mmol) of 1,3-cycloheptadiene was introduced into the flask followed by 5.2 mL (63 mmol) of diiodomethane. The flask was recharged with nitrogen and refluxed for 26 h. The mixture was cooled to room temperature and filtered into a separatory funnel. A 0.1 N HCl solution was slowly added and the ether washed two times with acid and once with water. The ether layer was dried ($MgSO_4$) and reduced under vacuum. Preparative GC (column temperature = 120 °C) yielded 2.7 g of **12a** as the 2nd fraction (43% yield): ^{1}H NMR ($CDCl_3$) 5.72 (m, 1 H), 5.38 (m, 1 H), 2.0 (m, 2 H), 1.85 (m, 1 H), 1.6 (m, 1 H), 1.45 (m, 2 H), 1.28 (m, 1 H), 1.12 (m, 1 H), 0.75 (ddd, 1 H), 0.1 (dd, 1 H); MS *m/e* (%) 108 (M^+, 33.6), 93 (75.7), 91 (90.9), 80 (55.9), 79 (100). HRMS: calcd for C_8H_{12}, *m/e* 108.0939; found, *m/e* 108.0954.

Formation of 12b. In a 5-dram vial were placed 61.7 mg (0.57 mmol) of **12a**, 4 mL of dry diethyl ether, and 161 mg (0.27 mmol) of Zeise's dimer. The mixture was stirred for 1 h at room temperature at which time a white precipitate had formed. The solid was filtered out and washed two times with 5 mL of pentane and dried under vacuum yielding 39 mg of **12b** (91% yield). Anal. Calcd for $C_{16}H_{24}Cl_4Pt_2$: C, 25.67; H, 3.21; Cl, 18.98. Found: C, 25.60; H, 3.16; Cl, 18.80. ^{1}H NMR ($CDCl_3$): 4.82 (dd, $J_{H,H}$ = 3.81, H-3), 4.73 (brd, 1 H), 4.66 (brd, 1 H), 1.3–2.1 (m, 9 H). ^{13}C NMR ($CDCl_3$): see Table II.

Formation of 13a. Cyclopropane **13a** was formed in a manner analogous to that for **11a** using 1,3-cyclooctadiene (65% yield): ^{1}H NMR[19] ($CDCl_3$) 5.67 (m, 1 H), 5.40 (brd, $J_{H,H}$ = 12, 1 H), 2.42 (m, 1 H), 1.95 (m, 3 H), 1.6 (m, 2 H), 1.2–1.45 (m, 2 H), 0.75–1.0 (m, 2 H), 0.7 (ddd, 1 H), −0.2 (dd, 1 H); ^{13}C NMR ($CDCl_3$) 134.5 (d), 126.7 (d), 31.3 (t), 29.6 (t), 28.0 (t), 25.8 (t), 19.2 (d), 14.6 (d), 10.5 (t). HRMS: calcd for C_9H_{14}, *m/e* 122.1095; found, 122.1115.

Formation of 13b. Zeise's dimer (124.7 mg, 0.21 mmol) was added to a 25-mL round-bottom flask containing 56.9 mg (0.46 mmol) of **13a** and solvent. The following conditions were tried: (A) Diethyl ether at room temperature for 8 h; (B) refluxing diethyl ether for 8 h; (C) refluxing chloroform under nitrogen for 18 h; (D) refluxing toluene for 2 h under nitrogen; (E) 250 mg of Zeise's dimer in refluxing diethyl ether for 10 h. The above experiments were all run with 10–15 mL of solvent with continuous stirring. At the end of the reaction pentane was added, precipitating an orange solid. The solid was generally washed a total of three times with pentane and then dried under vacuum. The precipitate was characterized by NMR in $CDCl_3$, which gave broad resonances due to the platinum. Addition of pyridine sharpened the signal and enabled platinum coupling to be measured. The pyridine solutions were unstable and decomposed to Py_2PtCl_2 and **13a** over a period of 8 h. Data for **13b**: ^{1}H NMR ($CDCl_3$) 5.8 (m, 1 H, $J_{Pt,C}$ = 70), 5.3 (dd, 1 H, $J_{Pt,C}$ = 69), 2.4–2.7 (m, 6 H), 1.55–1.85 (m, 3 H), 1.0 (m, 1 H), 0.7 (dd, 1 H), 0.2 (dd, 1 H); ^{13}C NMR ($CDCl_3$) 96.9 (d, $J_{Pt,C}$ = 152.6), 90.6 (d, $J_{Pt,C}$ = 156.0), 31.1 (t), 30.9 (t), 28.6 (t, 2 C), 22.9 (d), 14.9 (d), 13.6 (t).

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[19] Thies, R. W.; Hong, P. K.; Buswell, R.; Boop, J. L. *J. Org. Chem.* 1975, *40*, 585.

Notes

Identification of a Surface Organometallic Species Anchored on a Thiourea-Functionalized Silica Xerogel. Crystal Structure of the Model Compound $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$

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Summary: $Ru_3(CO)_{12}$ reacts with a thiourea-functionalized silica xerogel, derived from $(EtO)_3Si(CH_2)_3NHC({=}S)NHPh$, to give a tethered metal carbonyl cluster. This surface organometallic species has the same CO stretching pattern as that of the model compound $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$ (**1**), obtained from the reaction of $Ru_3(CO)_{12}$ with *N*-phenyl-*N'*-propylthiourea. The molecular structure of **1** has been fully elucidated by an X-ray diffraction study.

Transition-metal carbonyl clusters can be used both as heterogeneous catalyst precursors and as homogeneous catalysts themselves, for a variety of reactions.[1] Their immobilization by tethering to organic or inorganic solids yields systems that combine the advantages of both homogeneous and heterogeneous catalysts.[2] The active sites are discrete complexes, whose mechanism of action is similar to that of their truly homogeneous counterparts, but at the same time the ease of separation and recovery which characterize heterogeneous catalysts are retained. These systems have been prepared by a variety of routes, mostly inferred from organometallic solution chemistry of the suitable functional group present on the surface.[3] The phosphine group[4] anchored to silica is the most common

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(1) Johnson, B. F. G., Ed. *Transition Metal Clusters*; Wiley: Chichester, U.K., 1980. Gates, B. C., Guczi, L., Knözinger, H., Eds. *Metal Clusters in Catalysis*; Elsevier: Amsterdam, 1986.

(2) Bailey, D. C.; Langer, S. H. *Chem. Rev.* 1981, *81*, 109. Evans, J. *Chem. Soc. Rev.* 1981, *1*, 159. Gates, B. C.; Lieto, J. *CHEMTECH* 1980, 248.

(3) Gates, B. C. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; pp 415–424.

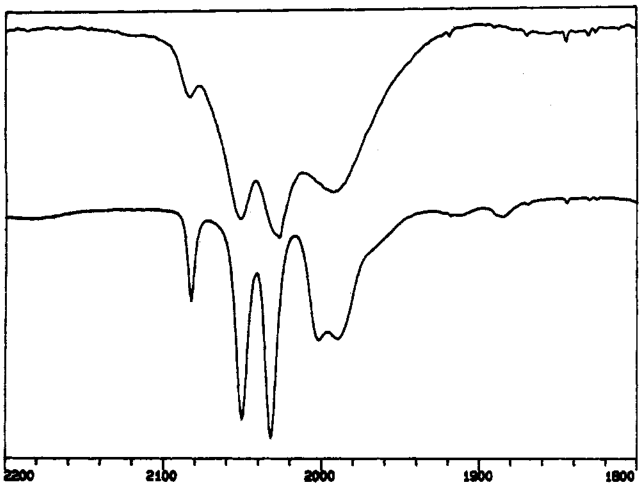

Figure 1. FT-IR spectra of (A, top) the anchored species (KBr) and (B, bottom) the model complex $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$ (1) (chloroform).

binding function, but nitrogen[5] and sulfur[6] donor ligands are suitable surface modifiers as well. They can be tethered to the inorganic oxide by the condensation reaction of surface Si–OH groups with $L\text{–}(CH_2)_n\text{–}Si(OR)_3$. Alternatively, it is possible to directly produce a functionalized silica xerogel by hydrolysis and co-condensation of $Si(OR)_4$ (4-fold cross-linking) and the suitable functionalized siloxane. This latter procedure gives robust materials with a higher content of available ligand groups than their silica-immobilized counterparts.[7]

We have recently found that a new thiourea-functionalized sol-gel material, derived from $(EtO)_3Si(CH_2)_3NHC(=S)NHPh$,[8] easily supports palladium(II) and metal carbonyl species by coordinative interactions. In the case of palladium, treatment with dihydrogen afforded well-dispersed nanoscale metal particles with high hydrogenating activity.[9]

In an effort to explore the coordinative capability of this functionalized material and possibly to produce new catalytic systems, we have reacted the xerogel with $Ru_3(CO)_{12}$.[10] The reaction must be carried out in a polar medium, as in hydrocarbons only physisorbed ruthenium carbonyl has been detected on the surface. The yellow solid obtained in 2-propanol exhibits the novel IR pattern reported in Figure 1A, suggesting the formation of the desired anchored species. Further evidence has come from the fact that the complex was not extracted by treatment with dichloromethane.

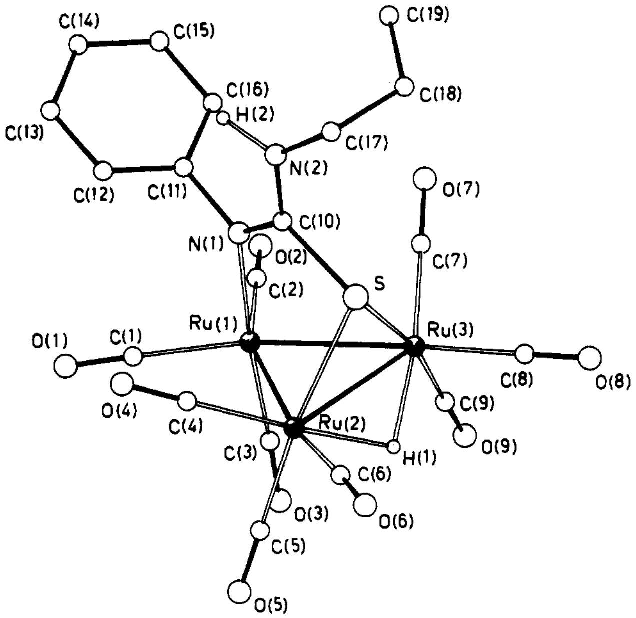

Figure 2. View of the molecular structure of $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$ (1). Important bond distances (Å) and angles (deg): Ru(1)–Ru(2) = 2.782 (1), Ru(1)–Ru(3) = 2.779 (1), Ru(2)–Ru(3) = 2.844 (1), Ru(1)–N(1) = 2.160 (6), Ru(2)–S = 2.404 (2), Ru(3)–S = 2.412 (2), S–C(10) = 1.786 (6), N(1)–C(10) = 1.285 (9), N(2)–C(10) = 1.351 (10), N(1)–C(11) = 1.449 (8), N(2)–C(17) = 1.452 (10); Ru(2)–Ru(1)–Ru(3) = 61.5 (1), Ru(1)–Ru(2)–Ru(3) = 59.2 (1), Ru(1)–Ru(3)–Ru(2) = 59.3 (1), Ru(2)–S–Ru(3) = 72.4 (1), Ru(2)–S–C(10) = 106.0 (2), Ru(1)–N(1)–C(11) = 120.9 (4), Ru(1)–N(1)–C(10) = 123.0 (4), C(11)–N(1)–C(10) = 116.1 (5), C(17)–N(2)–C(10) = 128.4 (6), N(1)–C(10)–N(2) = 125.0 (6), N(2)–C(10)–S = 115.5 (5), N(1)–C(10)–S = 119.6 (5).

In order to gain information on the tethered species, the non-siloxanized *N*-phenyl-*N'*-propylthiourea (a molecular model of the anchored ligand) has been synthesized and reacted with $Ru_3(CO)_{12}$. The reaction is rather clean, and the main product 1 is easily separated by thin-layer chromatography.[11] The ^1H and ^{13}C NMR spectra suggest that 1 is a hydridocarbonylruthenium cluster, containing a deprotonated thiourea. Its IR spectrum in the carbonyl stretching region (Figure 1B) is strictly comparable with that of the anchored species, even if the broadening of the bands in Figure 1A produces some differences between the two patterns, such as the collapse of the doublet observed at about 2000 cm^{-1} in the Figure 1B. However, this broadening is normally observed for anchored compounds compared to their model complexes and usually produces lack of resolution.[6,12] Even though we cannot exclude the presence of other minor species (e.g. one responsible for the appearance of a shoulder on the peak at 2029 cm^{-1} in Figure 1A) and of decomposition products (as the anchored

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(4) Castrillo, T.; Knözinger, H.; Wolf, M.; Tesche, B. *J. Mol. Catal.* 1981, *11*, 151. Evans, J.; Gracey, B. P. *J. Chem. Soc., Chem. Commun.* 1983, 247. Schubert, U.; Rose, K.; Schmidt, H. *J. Non-Cryst. Solids* 1988, *105*, 165. Schubert, U.; Egger, C.; Rose, K.; Alt, C. *J. Mol. Catal.* 1989, *55*, 330. Kiiski, U.; Pakkanen, T. A.; Krause, O. *J. Mol. Catal.* 1989, *50*, 143.

(5) Hilal, H. S.; Rabah, A.; Khatib, I. S.; Schreiner, A. F. *J. Mol. Catal.* 1990, *61*, 1.

(6) Catrillo, T.; Knözinger, K.; Wolf, M. *Inorg. Chim. Acta* 1980, *45*, L235. Evans, J.; Gracey, B. P. *J. Chem. Soc., Dalton Trans.* 1982, 1123.

(7) Khatib, I. S.; Parish, R. V. *J. Organomet. Chem.* 1989, *369*, 9.

(8) The thiourea-functionalized xerogel was easily prepared by hydrolysis and polycondensation of *N*-phenyl-*N'*-((triethoxysilyl)propyl)thiourea and tetraethoxysilane (1:10 volume ratio) in a water–ethanol mixture. The obtained xerogel was crushed, washed, and dried in vacuo: surface area 380 $m^2\ g^{-1}$ (BET method). Anal. Found: C, 8.3; H, 1.6; N, 2.0; S, 1.9. The FT-IR spectrum showed the characteristic bands of the thiourea fragment at 1556, 1502, 1454, and 697 cm^{-1}.

(9) Ferrari, C.; Predieri, G.; Tiripicchio, A.; Costa, M. *Chem. Mater.* 1992, *4*, 243.

(10) Anchoring of $Ru_3(CO)_{12}$: the functionalized silica xerogel (0.57 g) was added to a solution of $Ru_3(CO)_{12}$ (0.23 g) in 2-propanol (50 cm^3), under an N_2 atmosphere. The stirred solution was refluxed for 30 min. The brownish yellow suspended solid was filtered, washed, and dried in vacuo. FT-IR (KBr): 2083, 2051, 2029, 1992 cm^{-1}.

(11) Synthesis of 1: *N*-phenyl-*N'*-propylthiourea (0.15 g, 0.77 mmol) was added to a solution of $Ru_3(CO)_{12}$ (0.5 g, 0.78 mmol) in hexane (75 cm^3) under a nitrogen atmosphere. The solution was stirred under reflux for 40 min. TLC on silica gel yielded 0.3 g of 1 (red band), unreacted $Ru_3(CO)_{12}$, and traces of decomposition products. ^1H NMR (100 MHz, 295 K, $CDCl_3$): δ −12.94 (s, 1 H), 0.84 (t, J = 7.0 Hz, 3 H, CH_3), 1.46 (sex, J = 7.0, 2 H, CH_2), 3.37 (q, J = 6.7, 2 H, NCH_2), 4.51 (t, J = 6.2, 1 H, HN), 6.88–6.79 (m, 2 H, C_6H_5), 7.16–7.54 (m, 3 H, C_6H_5). $^{13}C\{^1H\}$ NMR (200 MHz, 295 K, $CDCl_3$): δ 10.69 (C(19)), 24.16 (C(18)), 48.59 (C(17)), 122.66 (C(13,15)), 126.89 (C(14)), 130.82 (C(12,16)), 149.02 (C(11)), 180.42 (C(10)), 196.54 (v br, 8 C, CO), 201.73 (1 C, CO). FT-IR (chloroform; cm^{-1}): CO 2082 (m), 2051 (s), 2032 (s), 2001 (m, br), 1990 (m, br). Anal. Calcd for $C_{19}H_{14}N_2O_9Ru_3S$: C, 30.4; H, 1.9; N, 3.7; S, 4.3. Found: C, 30.6; H, 2.0; N, 3.6; S, 4.2. In the presence of an excess of thiourea and for a longer reaction time, it was possible to isolate a second green product which exhibited more complex NMR spectra.

(12) Puga, J.; Fehlner, T. P.; Gates, B. C.; Braga, D.; Grepioni, F. *Inorg. Chem.* 1990, *29*, 2376.

Table I. Crystallographic Data for $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$

formula	$C_{19}H_{14}N_2O_9Ru_3S$
fw	749.60
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	16.093 (7)
b, Å	12.292 (5)
c, Å	14.058 (5)
β, deg	113.81 (2)
V, Å^3	2544 (2)
Z	4
μ(Mo Kα), cm^{-1}	18.52
d_{calc}, g cm^{-3}	1.957
diffractometer	Philips PW 1100
2θ range, deg	6–50
no. of unique rflns collected	4740
no. of rflns with $I > 2\sigma(I)$	2737
R	0.0242
R_w	0.0304
no. of variables	327

compound turns into other surface carbonyl species in a few hours in the air), nevertheless the overall matching of the bands of spectra A and B in Figure 1 strongly suggests the presence on the xerogel of a tethered compound similar to 1 as the major species.

The structure of 1, fully elucidated by an X-ray study,[13] can be formulated as $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NHPr)NPh}\}(CO)_9]$. A view of it is depicted in Figure 2 together with the atomic labeling scheme and the most important bond distances and angles.

The structure displays a triangular cluster of Ru atoms, each of which is bound to three terminal carbonyls. The deprotonated (on the nitrogen atom N(1) bound to the phenyl group) thiourea ligand interacts with all three Ru atoms; in fact, it is bonded through the N(1) atom to Ru(1) and through the sulfur atom (acting as a symmetrical bridge) to the other two Ru atoms. The hydrogen atom, shifted by N(1), acts as a hydridic bridge on the longest edge of the cluster, on which also the sulfur bridge is disposed. The two bridges form dihedral angles of 128 (2) and 100.8 (1)°, respectively, with the cluster triangle.

The value of the S–C(10) bond distance (1.786 (6) Å) is in agreement with a remarkable decreasing of double-bond character, being much longer than that found in complexed and in free substituted-thiourea molecules (mean values 1.725 (19)[16] and 1.681 (20) Å,[17] respectively). In $[(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-SEt})]$, in which the sulfur of the thiolate ligand bridges an edge of the Ru cluster (Ru(2)–S = 2.389 (4) Å and Ru(3)–S = 2.391 (4) Å) in the same way, the C–S bond distance is slightly longer (1.834 (13) Å).[18] The values of the N(1)–C(10) and N(2)–C(10) bond lengths (1.285 (9) and 1.351 (10) Å, respectively) are rather different, indicating an increased multiple-bond character for the former, namely that involving the deprotonated N(1) atom, whereas they are practically equal in complexed and in free substituted-thiourea molecules (mean values 1.322 (16)[16] and 1.346 (23) Å,[17] respectively).

To our knowledge, 1 is the second example of a carbonylmetal cluster containing an *intact* (even though deprotonated) substituted thiourea. In fact, very recently, it has been found that, from the reaction between $Ru_3(CO)_{12}$ and symmetrically substituted thioureas, very similar complexes $[(\mu\text{-H})Ru_3\{\mu_3\text{-SC(NR}_2\text{)NR}\}(CO)_9]$ have been obtained when R = H, Me, and Ph,[19] whereas with *N*,*N*′-di-*tert*-butylthiourea, two complexes, $[(\mu\text{-H})Ru_3(\mu_3\text{-S})(\eta^2\text{-CH}_2\text{CMe}_2\text{NHCNH}^t\text{Bu})(CO)_8]$ (2) and $[(\mu\text{-H})Ru_3\{\mu_3\text{-SRu(CO)}_3(\eta^2\text{-CH}_2\text{CMe}_2\text{NHCNH}^t\text{Bu})\}(CO)_9]$ (3), have been isolated and structurally characterized.[20] In complexes 2 and 3 the *N*,*N*′-di-*tert*-butylthiourea molecule is formally cleaved into a sulfur fragment and a diaminocarbene moiety, both interacting with ruthenium atoms. Furthermore, a hydrogen atom from a *tert*-butyl group is shifted as the bridge on an edge of the cluster with coordination of the resulting CH_2 unit to a Ru atom. In 2 sulfur acts as a triple bridge, being bonded to all three Ru atoms, and the diaminocarbene behaves as a chelating ligand, being bound to one Ru atom through the diamino and methylene carbon atoms. In 3 sulfur caps the Ru_3 triangle and is also bound to a fourth Ru atom of a $Ru(CO)_3$ fragment.

In conclusion, from the structural characterization of 1, it was possible to identify an anchored species obtained by reaction between a thiourea-functionalized xerogel and $Ru_3(CO)_{12}$ in 2-propanol. These results have stimulated further investigations on the coordinative capability of substituted thioureas toward metal carbonyl clusters and on the catalytic properties of the resulting systems.

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Registry No. 1, 143039-20-7; $Ru_3(CO)_{12}$, 15243-33-1.

Supplementary Material Available: Tables of coordinates for the non-hydrogen atoms (Table SI) and for hydrogen atoms (Table SII), anisotropic thermal parameters for the non-hydrogen atoms (Table SIII), and all bond distances and angles (Table SIV) (4 pages). Ordering information is given on any current masthead page.

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(13) Crystal data for 1: The crystallographic data are summarized in Table I. Accurate unit cell parameters were determined from the θ values of 30 carefully centered reflections. Data were collected at room temperature on a Philips PW 1100 diffractometer, using graphite-monochromated Mo Kα radiation and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed at 3–12° min^{-1} and a scan width from $(\theta - 0.65)°$ to $(\theta + 0.65 + 0.346 \tan \theta)°$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects, but no absorption correction was necessary. The structure was solved by direct and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms, except the hydridic H(1) and the hydrogen bound to N(2), which were clearly localized in the final ΔF map and refined isotropically, were placed at their geometrically calculated positions (C–H = 1.08 Å) and refined "riding" on the corresponding carbon atoms. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the K and g values were 0.714 and 0.002, respectively. The analytical scattering factors, corrected for anomalous dispersions, were taken from ref 14. All calculations were carried out on the Cray X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould POWERNODE 6040 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[15]

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(15) Sheldrick, G. M. SHELX-76 Program for Crystal Structure Determination; University of Cambridge: Cambridge, U. K., 1976. SHELXS-86 Program for the Solution of Crystal Structures; University of Göttingen: Göttingen, Germany, 1986.

(16) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(17) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(18) Churchill, M. R.; Ziller, I. W.; Keister, J. B. *J. Organomet. Chem.* **1985**, *297*, 93.

(19) Bodensieck, U.; Stoeckli-Evans, H.; Süss-Fink, G. *Chem. Ber.* **1990**, *123*, 1603.

(20) Bodensieck, U.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc., Chem. Commun.* **1990**, 267.