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Synthesis and chemistry of 1-acetyl, 2-methylsubstituted cyclopentadienyl thallium and its chiral manganese and rhodium carbonyl derivatives. The molecular structure of [1-CH_3CO, 2-$CH_3C_5H_3$]Rh(CO)[$P(C_6H_5)_3$]

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Abstract

Reaction of sodium methylcyclopentadienide and ethyl acetate yields a 1:1 mixture of the sodium salts of 1-acetyl, 2-methylcyclopentadienide, **1**, and its 1-acetyl, 3-methyl isomer, **2**. Reaction of this mixture with thallium ethoxide yields the corresponding thallium salts from which pure 1-acetyl, 2-methylcyclopentadienyl thallium, **3**, can be obtained by fractional crystallization from ethanol. Isomerically enriched samples of 1-acetyl, 3-methyl thallium compound, **4**, can be obtained from the recrystallization filtrates. Reaction of **3** with $BrMn(CO)_5$ yields the planar chiral complex 1-acetyl, 2-methylcymantrene, **5**, as a racemic mixture. Reaction of **3** with $[ClRh(CO)_2]_2$ gave 1-acetyl, 2-methylcyclopentadienyl rhodium dicarbonyl, **6**. Reaction of thallium mixtures enriched in **4** with $[ClRh(CO)_2]_2$ yields, after chromatography, small samples of 1-acetyl, 3-methylcyclopentadienyl rhodium dicarbonyl, **10**. A small quantity of a dinuclear complex, **7**, was obtained from **6** and shown to consist of both the *meso* and *racemic* forms of **7**. Reaction of **6** with trimethylamine oxide yielded a trinuclear complex, **8**, whose spectra and chiral HPLC are fully consistent with the expected distribution of isomers for a *triangulo* complex with three chiral centers. **6** reacts with triphenylphosphine to give the expected carbonyl, triphenylphosphine derivative, **11**, which was crystallographically characterized: $C_{27}H_{24}O_2PRh$, monoclinic, $P2_1/c$, $a = 9.029(1)$, $b = 11.196(2)$, $c = 23.298(4)$ Å, $\beta = 91.34°$, $V = 2354.7$ Å^3, $Z = 4$, $R(F) = 3.65\%$. Oxidative addition of iodomethane with **11** gives a diastereomeric mixture of cyclopentadienylrhodium(acetyl)iodo(triphenylphosphine) isomers, **12**, in an approximately 1:2 ratio indicating modest chiral induction by the ring substituents of addition at the metal. Chiral HPLC using columns of CHIRALCEL OD are described for several of the racemic mixtures.

Introduction

When a metal group is π bonded to a 1-, 2- or 1-,3-asymmetrically disubstituted cyclopentadienyl or arene ring, the resulting complex exhibits planar chirality.

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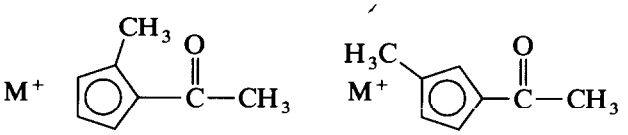
Numerous examples of organometallic complexes in these two categories have been reported, and Brunner has twice reviewed this area [1]. In keeping with our interest in expanding the availability of ring-functionalized cyclopentadienyl thallium synthons [2], we wish to report the synthesis of 1-acetyl, 2-methylcyclopentadienyl thallium and its 1-,3-isomer, and describe the use of the 1,2-disubstituted reagent in the synthesis of rhodium and manganese complexes. A recent publication by Vollhardt and coworkers describes the synthesis of 1,2- and 1,3-methylcarboxylate, methylcyclopentadienyl cobalt complexes by a procedure very similar to those reported in this paper [3].

Results and discussion

Sodium methylcyclopentadienide, formed from methylcyclopentadiene with either sodium dispersion or sodium hydride in THF, was reacted with ethyl acetate as has been previously reported for the synthesis of sodium acetylcyclopentadienide [4]. Upon concentration of the reaction mixture, a light tan solid was isolated which was shown by NMR to be a 1:1 mixture of the 1,2- and 1,3-disubstituted



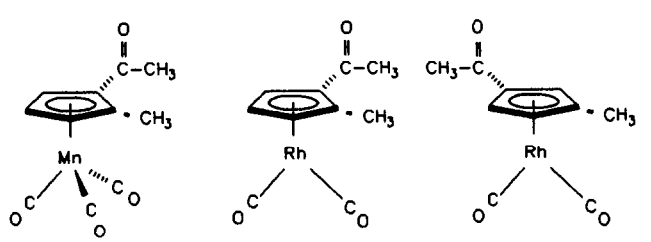
1: M = Na **2**: M = Na

3: M = Tl **4**: M = Tl

isomers, **1** and **2**, respectively. Reaction of the mixture of **1** and **2** with thallium ethoxide yields a 1:1 mixture of the thallium salts, **3** and **4**, respectively, as a tan solid, from which **4** can be substantially removed by recrystallization from ethanol. Some **3** is lost in this process. **3** can be obtained free of **4** by this technique, however, it has not been possible to recover a pure sample of **4**. Both **3** and **4** are slightly air and light sensitive and should be stored under nitrogen in the dark. As with all thallium compounds, these materials should be handled with rigorous safety precautions.

^1H and ^{13}C NMR of **3** and **4**, and IR of **3** are unexceptional and consistent with the proposed structures.

Reaction of the 1:1 mixture of **3** and **4** with $BrMN(CO)_5$ in refluxing benzene gives a mixture of cymantrene derivatives which could be resolved by HPLC on



5 **6** **10**

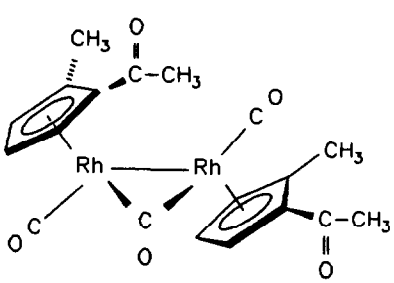
silica gel but not by conventional or medium pressure column chromatography. A sample of 1-acetyl,2-methyl cymantrene, **5**, was obtained as a crystalline solid in good yield by reaction of pure **3** with $BrMn(CO)_5$. Again, the spectra are consistent with the proposed structures. IR stretching frequencies of the metal carbonyl (2027 and 1945 cm^{-1}) and acetyl groups (1682) are shifted slightly to lower energy relative to acetylemantrene [5] (2031, 1950 and 1685, respectively) owing to the electron donating methyl group. The EI mass spectrum of **5** contains a strong M^+ signal and the expected metal-carbonyl loss cascade. $M^+ - 3$ CO is the base peak and strong signals are observed for Mn^{1+} and $MnCH_3^{1+}$. In contrast to our observations with acetylcymantrene, **5** appears to be quite light sensitive, decomposing to give an insoluble solid on long exposure to light on the bench top. We tentatively suggest that this observed light sensitivity is due to a Norrish II phototautomerization in which a methyl proton is transferred to the acyl oxygen [6]. Work on the photolysis of this and other ring substituted cymantrene complexes is proceeding in this laboratory.

As with the cymantrene synthesis, reaction of the 1:1 mixture of **3** and **4** with $[ClRh(CO)_2]_2$ gave a mixture of 1,2- and 1,3-disubstituted cyclopentadienyl rhodium dicarbonyl isomers which could not be readily separated by chromatography. Again, reaction of purified **3** with $[ClRh(CO)_2]_2$ gave 1-acetyl, 2-methylcyclopentadienyl rhodium dicarbonyl, **6**, in good yield.

A small sample of **4** containing **3** as an impurity was reacted with $[ClRh(CO)_2]_2$ and gave a mixture of disubstituted cyclopentadienyl rhodium dicarbonyl isomers which was successfully separated by chromatography on alumina to give a small amount of 1-acetyl, 3-methylcyclopentadienyl rhodium dicarbonyl, **10**.

^1H and ^{13}C NMR of **6** and **10** are consistent with the proposed structures. Comparison of the infrared stretching frequencies of both the metal carbonyl and acetyl groups of **6** and **10** with those of acetylcyclopentadienyl rhodium dicarbonyl shows that the absorbencies of **6** and **10** are shifted slightly to lower energy. As with the cymantrene derivative, this shift can be attributed to the donation of electron density by the ring methyl group.

HPLC of **6** and **10** on an analytical CHIRALCEL OD column using heptane: i-propanol as an eluant gave baseline separation of the optical isomers of **6** but **10** was not resolved. An α value of 1.25 was calculated for **6**.



7

On extended storage at room temperature, **6** gave rise to a red solid which was found by HPLC to consist of two components. This material was shown to be a mixture of isomers of the complex, **7**, which was readily identified as a dinuclear complex by its IR spectrum consisting of a strong asymmetric terminal carbonyl

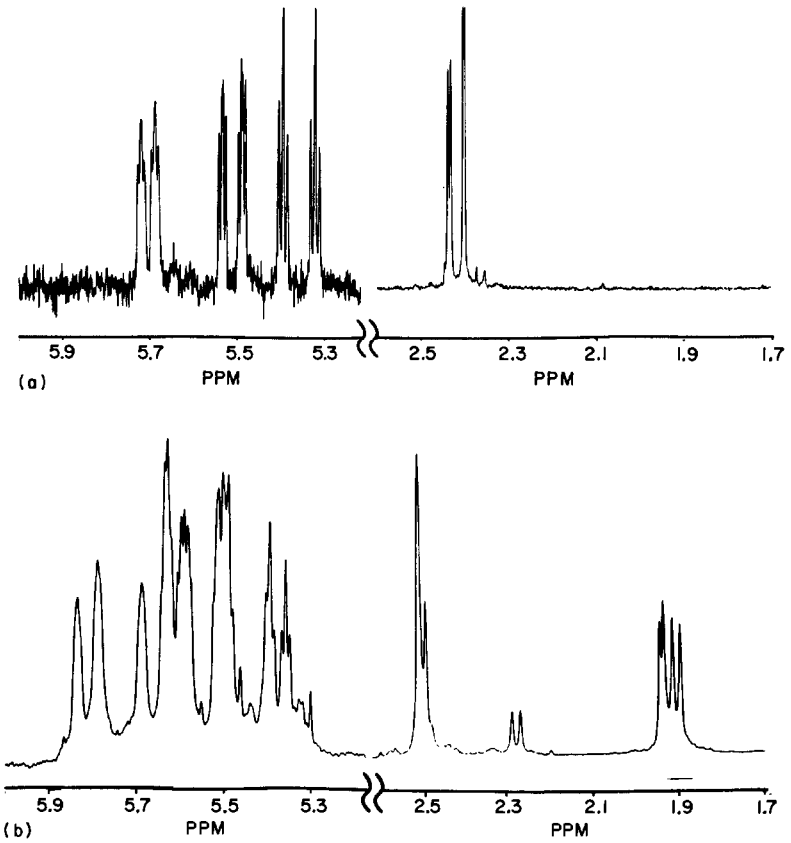
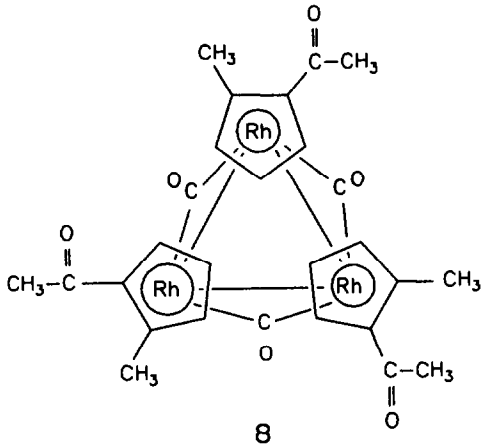


Fig. 1. Ring hydrogen and methyl hydrogen regions of the ^1H NMR spectrum of (a) **7** and (b) **8**.

stretch and a bridging carbonyl stretch. A weak symmetric metal carbonyl stretch is also observed as is a band characteristic of the acetyl group. Assuming a statistical distribution, a racemic mixture of **6** would be expected to give rise to a 1 : 1 mixture of meso and racemic dinuclear complex. The ^1H (Fig. 1a) and partial ^{13}C NMR spectra (only C–H ring carbons, acetyl methyl, and ring methyl groups were observed) are fully consistent with the presence of two isomers in equal concentration. Attempted separation of this mixture on a CHIRALCEL OD HPLC column gave two bands with 1 : 3 relative area. We believe that one of the enantiomers of the racemic mixture is eluting simultaneously with the meso isomer to produce the observed chromatogram. We have been unable to identify conditions which will cleanly resolve the *meso* and *racemic* forms of this material.

On standing, **7** loses carbon monoxide to give a small quantity of a purple complex which was separated from **7** by chromatography. IR spectroscopy of the very small sample of this purple material reveals a group of ill-defined low energy bands which are almost identical in position to those reported for $[CpRh(CO)]_4$ by Lawson and Shapley [7]. These IR features and the characteristic color of the compound support our assignment of this material as the tetranuclear derivative, **9**, of **6**. It is perhaps significant that no green trinuclear derivative was observed

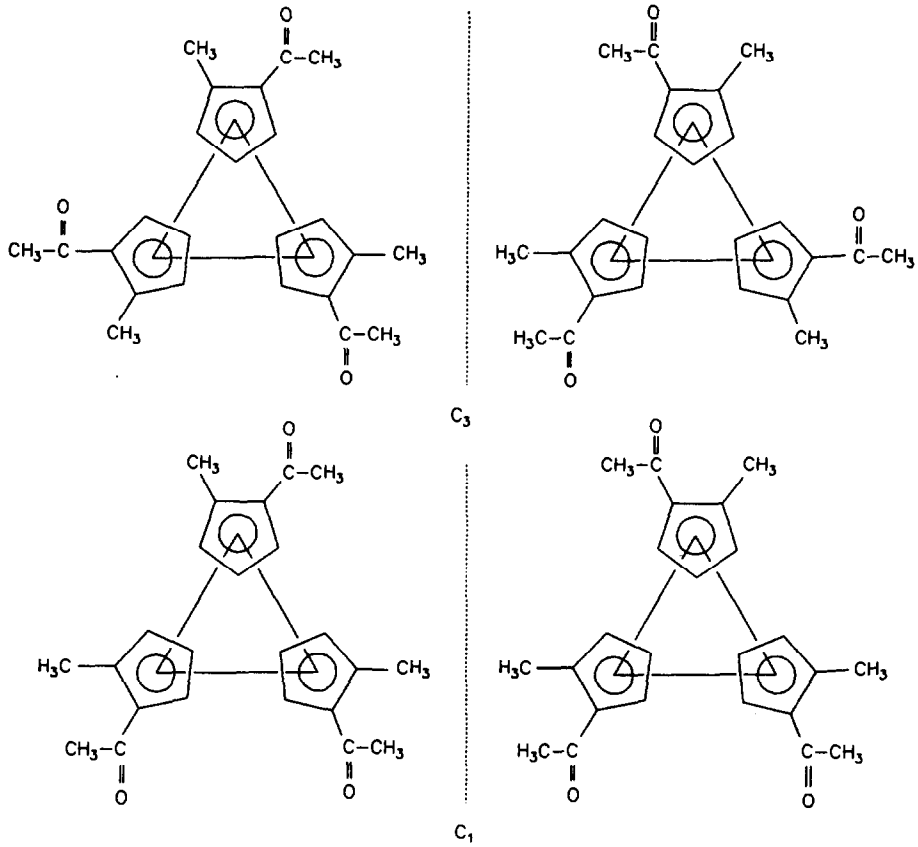


8

arising from **7** suggesting that **7** can itself dimerize to give rise to the tetranuclear form.

Reaction of **6** with excess trimethylamine oxide in benzene results in the formation of the green trinuclear complex, **8**, as the sole product of the reaction. **8** was identified as the trinuclear derivative of **6** by its IR spectrum which is almost identical to that of $[CpRh(CO)]_3$ reported by Lawson and Shapley [7]. These workers argued that the overall symmetry of $[CpRh(CO)]_3$ must be C_{3v} on the basis of the IR spectral pattern of the bridging carbonyl bands, and this structure has been confirmed by X-ray crystallography [8]. In a C_{3v} *triangulo* species all three cyclopentadienyl rings must be on the same side of the rhodium triangle. Substituting an asymmetrically disubstituted cyclopentadienyl ring for C_5H_5 gives rise to two racemic mixtures, SSS/RRR, and SSR/RRS which are predicted to form in a 1:3 ratio. These isomers are illustrated in Scheme 1. HPLC of this mixture on CHIRALCEL OD gives rise to a pair of bands followed by a broad large band. The relative areas suggest that the pair of bands represent the resolved *SSS* and *RRR* isomers, with the larger, broad band being the unresolved *SSR* and *RRS* isomers.

Examination of the isomers illustrated in Scheme 1 allows a prediction of the NMR spectra of these isomers. The C_3 symmetry of the *SSS* and *RRR* isomers is predicted to give rise to three C–H ring resonances in the ^{13}C spectrum and a single resonance each for the acetyl and methyl hydrogens in the ^1H spectrum. In contrast, the C_1 symmetry of the *SSR* and *RRS* isomers would be expected to give rise to nine different ring C–H environments, and three different acetyl and methyl hydrogen environments, excluding accidental overlap of resonances. Since the C_3 and C_1 isomers are present in a 1:3 ratio, theory predicts twelve equivalent C–H ring carbon resonances and four equivalent acetyl and methyl hydrogen resonances. Analysis of the actual spectra of **8**, Figs. 1b and 2, reveals exact agreement to theory with twelve equivalent C–H ring carbon resonances in the ^{13}C spectrum, and four equivalent methyl resonances in the ^1H spectrum. Accidental overlap reduces the acetyl resonances to two singlets with a relative integration of 3:1. The ring proton resonance pattern for **8** is complex. We suggest that the



Scheme 1.

overall structure of **8** is identical to that of C_{3v} $[CpRh(CO)]_3$, and is, to the best of our knowledge, the first demonstration of the use of chiral cyclopentadienyl–metal moieties to establish the geometry of a polynuclear species.

Reaction of **6** with triphenylphosphine in refluxing benzene resulted in efficient exchange of triphenylphosphine for carbonyl to give a quantitative yield of 1-acetyl, 2-methylcyclopentadienylrhodium(carbonyl)triphenylphosphine, **11**, as a red solid. HPLC of the racemic mixture of this compound on the CHIRALCEL OD column gave baseline separation with an α value of 2.17.

Conventional 1-D ^1H, ^{13}C, and ^{31}P NMR spectra of **11** were recorded along with 2-D COSY, and NOESY spectra. This battery of techniques was employed to firmly establish the connectivity of the ring protons, and to determine, to the greatest extent possible, the solution phase geometry of the molecule. Additional spectral comparisons were made with acetylcyclopentadienyl rhodium dicarbonyl and its triphenylphosphine derivative which were prepared in connection with other programs in this laboratory [9].

^1H NMR of the ring proton region of **11** reveals three resonances which were assigned to H-4, H-3, and H-5, respectively. H-5 was found by COSY to weakly couple with the acetyl methyl group, and its proximity to the acetyl group was

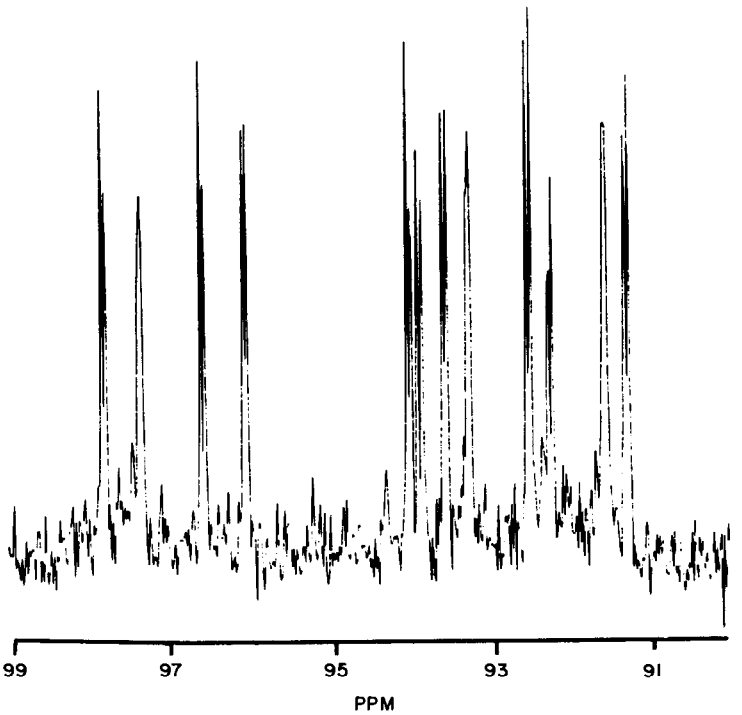
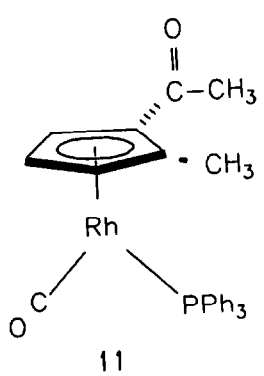


Fig. 2. Ring carbon region of the ^{13}C NMR spectrum of **8**.

confirmed by NOE. The ring methyl group is split into a doublet by coupling with the phosphine. Similar couplings have been observed for ring methyl groups in 1-methyl, 2-phenyl- and 1-methyl, 3-phenylcyclopentadienylrhodium(carbonyl)triphenylphosphine [9].

Of particular relevance to a conformational argument, is the strong upfield shift of the acetyl methyl which is found *above* the ring methyl in the proton spectrum. The ring and acetyl methyl groups are both shown by NOSY to interact with the phenyl groups of the triphenylphosphine ligand. In the solid state structure of **11** to



11

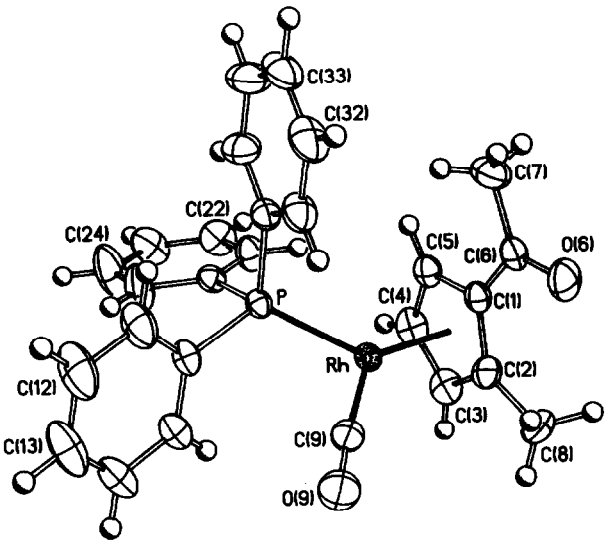


Fig. 3. General perspective of **11**.

be discussed below, the methyl of the acetyl group is found to be positioned almost above one of the phenyl groups of the triphenylphosphine, but the ring methyl group is quite far away. For both the acetyl and ring methyl groups to interact with the triphenylphosphine there must be free rotation about the rhodium to ring bond in solution.

An X-ray crystal structure of **11** was carried out to confirm the connectivity of the ring substituents. This structure is shown in Figs. 3 and 4. The CO–Rh–PPh_3 bond angle is 92.3(1)°, close to the expected 90° angle and chemically equivalent to the 90.6° angle observed for $(\eta^5,\eta^5\text{-}C_{10}H_8)[Rh(CO)PPh_3]_2$ reported by Orpen *et al.* [10]. Rh–CO and Rh–P bond lengths in **11**, 1.829(4) and 2.263(1) Å, compare closely with those reported for the dinuclear complex, 1.808(7) and 2.255(1) Å. Of particular interest is the relative orientation of the ring to the plane defined by the phosphine, rhodium and carbonyl. As shown in Fig. 4, the ring is oriented so that the acyl group is almost 90° to this plane. Furthermore, the ring bonds C(2)–C(3) and C(4)–C(5) are elongated slightly suggesting an allyl–ene bonding mode for the cyclopentadienyl group. A similar geometry has been observed by Rausch and coworkers [11] for $NO_2CpRh(CO)_2$, and allyl–ene ring distortions have been observed for the series, $(\eta^5\text{-}C_5Me_5)M(CO)_2$ where M = Co, Rh, and Ir [12].

Reaction of a racemic mixture of **11** with iodomethane gave the expected addition product as a mixture of diastereomers, **12**. IR, ^1H and ^{13}C NMR spectroscopy reveal the presence of two different acetyl groups, one ring-bound and the second metal-bound. Both ^1H and ^{31}P NMR of this mixture indicates that the diastereomers are formed in a 60:40 ratio suggesting that the ring substituents are directing the orientation of attack on the metal to a modest degree.

An analysis of the ^1H and ^{13}C spectra has made it possible to assign resonances to the two diastereomers. In the case of the major isomer, the resonance of the ring acetyl group has shifted to below that of the ring methyl group, whereas in the lesser isomer this resonance remains above. Regrettably we have not been able to

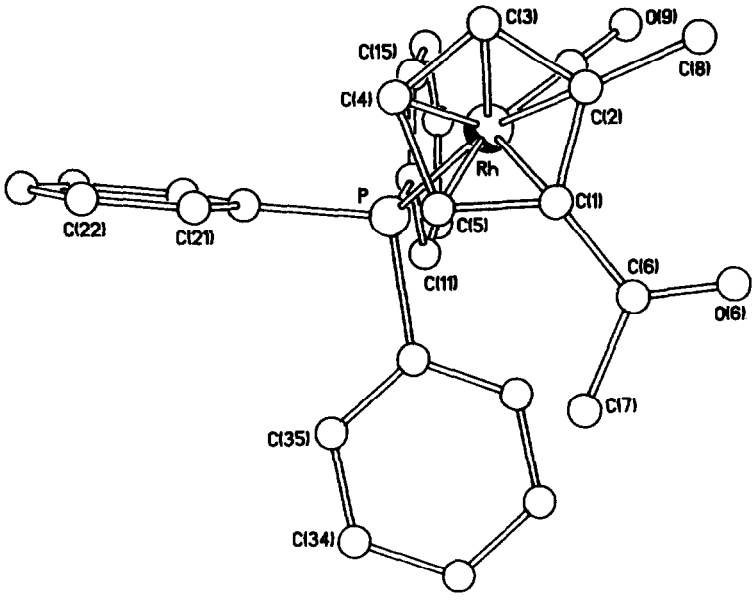
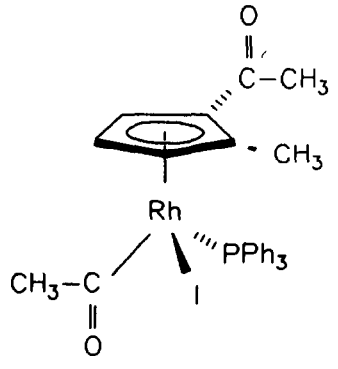


Fig. 4. View of **11** down the Rh–ring centroid axis.

carry out preparative scale separations of this diastereomeric mixture nor obtain pure crystals of one isomer. However, the diastereomeric mixture was chromatographed on the CHIRALCEL OD column and gave baseline separation of all four components of the mixture.

Attempts to expand this chemistry to the synthesis of other asymmetrically disubstituted cylopentadienyl complexes is now in progress. Preliminary results indicate that the analogous methyl, ethylcarboxylatecyclopentadienyl thallium compounds are formed in 1:1 mixtures of the 1,2- and 1,3-isomers which have not yet



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been successfully separated into pure components. Work on these and related asymmetrically disubstituted cyclopentadienyl ring complexes is continuing.

Experimental

Methylcyclopentadiene dimer was purchased from Aldrich and thermally cracked into an ice cooled receiver. Methylcyclopentadiene was stored for several months at −78°C with no apparent reversion to the dimer. Thallium ethoxide [13] and $[ClRh(CO)_2]_2$ [14] were prepared by standard literature routes. **NOTE**: Thallium compounds are highly toxic and must be handled with rigorous safety precautions. All solvents were dried and distilled under nitrogen. Preparative chromatography was conducted using nitrogen flushed solvents and neutral (CAMAG) alumina. Chiral chromatography was conducted on a CHIRALCEL OD analytical column using nitrogen flushed 5% isopropanol in heptane as an eluant.

Infrared spectra were recorded on a Bio-Rad Qualimatic FTIR Spectrometer operating at 2 cm^{-1} resolution. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on an IBM NR-300 MHz NMR Spectrometer and were referenced to appropriate solvent resonances (^1H and ^{13}C) or external 85% phosphoric acid (^{31}P). 2-D NMR spectra and mass spectroscopy were carried out by Dr. Gary Knerr of the University of Idaho. Electron impact, chemical ionization, and high resolution mass spectroscopies were recorded on a VG 7070-HS GC/MS using direct insertion. Elemental analyses were conducted by Desert Analytics of Tucson, AZ.

Synthesis of 1-acetyl, 2-methyl-, and 1-acetyl, 3-methyl-sodium cyclopentadienide, 1 and 2

Cracked methylcyclopentadiene (14.80 g, 0.186 mol) was added dropwise to a suspension of sodium hydride (4.45 g, 0.193 mol) in THF (200 mL) under nitrogen. After formation of sodium methylcyclopentadienide was complete, ethylacetate (16.40 g, 0.186 mol) was added rapidly and the mixture refluxed overnight. The reaction mixture was allowed to cool to room temperature and the solvent reduced to about 40 mL. Addition of ethyl ether (100 mL) resulted in the immediate formation of a granular tan solid which was filtered using a Schlenk filter. After washing the solid with ethyl ether, solvent was removed under vacuum to give 2.79 g of a mixture of **1** and **2**. Yield: 10%.

Synthesis of 1-acetyl, 2-methylcyclopentadienylthallium, 3, and 1-acetyl, 3-methylcyclopentadienylthallium, 4

The mixture of **1** and **2** (2.79 g, 19.4 mmol) from above was taken up in ethanol (50 mL) under nitrogen, and thallium ethoxide (4.82 g, 19.35 mmol) was added dropwise with stirring. A tan precipitate formed during this addition. The mixture was allowed to react for three hours and then filtered. ^1H NMR of the recovered tan solid indicated that it consisted of 80% **3** and 20% **4**. The filtrate was stripped of solvent and an additional quantity of tan solid recovered. ^1H NMR analysis of this material showed it to be 40% **3** and 60% **4**. Recrystallization of mixtures of **3** and **4** from ethanol yields samples of **3** which are free of **4**.

NMR spectra of **3** were recorded on an isomerically pure sample. ^1H NMR: (dmso-d_6) 6.12 (d of d, 1 H), 5.55 (broad t, 1 H), 5.42 (t, 1 H), 2.23 (s, 3 H), 2.11 (s,

3 H). ^{13}C NMR: (dmso-d_6) 189.8 ($COCH_3$), 123.8 (*ipso* Cp), 121.7 (*ipso* Cp), 113.2 (Cp), 113.0 (Cp), 107.7 (Cp), 27.4 ($COCH_3$), 16.4 (CH_3). IR: (Nujol) 1584 cm^{-1}. Analysis. * Found: 31.10; H, 3.36. C_8H_9OTl calc.: C, 29.50; H, 2.27%.

NMR spectra of **4** were recorded on a mixture of isomers. ^1H NMR: (dmso-d_6) 6.05 (d of d, 1 H), 5.85 (m, 1 H), 5.35 (m, 1 H), 2.02 (s, 3 H), 1.96 (s, 3 H).

Synthesis of 1-acetyl, 2-methylcymantrene, 5

A sample of **3** which was shown by NMR to be free of traces of **4** was used in this synthesis. **3** (0.60 g, 2.04 mmol) and $BrMn(CO)_5$ (0.56 g, 2.04 mmol) were taken up in benzene and refluxed overnight. After filtration through Celite, the solvent was removed using a rotary evaporator and the resultant oil was chromatographed on alumina using 1:1 dichloromethane:petroleum ether. A light yellow band, identified as $Mn_2(CO)_{10}$ by IR, was rapidly eluted from the column. Continued elution recovered a dark yellow band. Removal of solvent from this band gave 0.370 g of **5** as a dark red oil which crystallized after being stored at −78°C for several days. Yield: 70%. Mp: 44.5–46.0°C. IR: (CH_2Cl_2) 2027 (s, Mn–CO), 1945 (s, Mn–CO), 1682 (m, $COCH_3$). ^1H NMR: ($CDCl_3$) 5.21 (broad s, 1 H), 4.64 (broad s, 2 H), 2.25 (broad s, 3 H), 2.19 (broad s, 3H). ^{13}C NMR: ($CDCl_3$) 223.2 (Mn–CO), 196.6 ($COCH_3$), 106.8 (*ipso* Cp), 87.2 (Cp), 85.3 (Cp), 80.5 (Cp), 27.7 ($COCH_3$), 14.0 (CH_3) (the second *ipso* ring carbon was not located). Mass spectroscopy: (EI mode) 260 (22.7, M^+); 246 (1.4, $M^+ - CH_2$); 204 (17.0, $M^+ - 2$ CO); 176 (100.0, $M^+ - 3$ CO); 162 (5.4, $M^+ - 3$ CO and CH_2); 148 (1.7, $M^+ - 4$ CO); 132 (4.9, $M^+ - 3$ CO and H_2CO); 70 (54.1, $MnCH_3^+$), 54.9 (68.0, Mn^+). High resolution mass spectroscopy: found: 259.9888; calc.: 259.9881; error = 2.6 ppm.

Synthesis of 1-acetyl, 2-methylcyclopentadienyl rhodium dicarbonyl, 6, and its dinuclear, 7, and tetranuclear, 9, derivatives

A sample of **3** which was free of traces of **4** was used in the synthesis. **3**, 1.50 g, 4.61 mmol) and $[ClRh(CO)_2]_2$ (1.0 g, 2.57 mmol) were allowed to react overnight in refluxing benzene under nitrogen. The reaction mixture was filtered through Celite while still warm to give a dark red solution. The solvent was removed using a rotary evaporator and the resulting red oil chromatographed on alumina using 20% dichloromethane in petroleum ether. A red-brown band was eluted which was collected under nitrogen. Removal of solvent gave 0.70 g of **6** as a red-brown oil. Yield: 54%. IR: (CH_2Cl_2) 2053 (s, Rh–CO), 1992 (s, Rh–CO), 1663 (m, $COCH_3$). ^1H NMR: ($CDCl_3$) 5.42 and 5.33 (2 H, multiplet), 5.47 (1 H, d of t, $J(t) = 2.85$, $J(d) = 0.90$ Hz) 2.37 (s, 3 H), 2.35 (s, 3 H). ^{13}C NMR: ($CDCl_3$) 192.8 ($COCH_3$), 188.8 (Rh–CO, $J(Rh–C) = 83.9$ Hz), 107.4 (*ipso* Cp), 104.5 (*ipso* Cp), 95.0 (Cp, J-(Rh–C) = 3.5 Hz) 88.9 (Cp, J(Rh–C) = 3.8 Hz), 86.0 (Cp J (Rh–C) = 3.6 Hz), 27.5 ($COCH_3$), 14.8 (CH_3). Mass spectrometry: (EI) 280 (49.9, M^+), 252 (78.9, $M^+ -$ CO), 224 (100.0, $M^+ - 2$ CO), 222 (14.7, $M^+ -$ CO and CH_2O), 196 (21.8, $M^+ - 3$ CO), 194 (73.2, $M^+ - 2$ CO and CH_2O), 181 (48.8, $RhC_6H_6^+$). Chiral HPLC: (0.5 mL/min) $t_{R1'} = 12.0$ min, $t_{R2'} = 15.0$ min, $\alpha = 1.25$. High resolution MS: $C_{10}H_9O_3Rh$ found: 279.9607; calc.: 279.9607; error = 3 ppm.

* NMR has shown that the compound tenatiously retains ethanol which is undoubtedly responsible for the analysis error.

Continued elution of the column using neat dichloromethane yielded a red band which was stripped of solvent to give approximately 15 mg of **7** as a red solid. Analytical HPLC chromatography of a sample of this material resolved two components of roughly equal concentration (based on relative areas) which were assumed to be due to the *meso* and *racemic* mixtures. Chromatography using the chiral column gave two bands in a 1:3 ratio. The first of these bands was attributed to one of the enantiomers, and the second band to the remaining enantiomer eluting simultaneously with the *meso* complex. It was not possible to resolve this second enantiomer from the *meso*. IR: (CH_2Cl_2) 2033 (w, Rh–CO), 1994 (s, Rh–CO), 1830 (w, μ-CO), 1663 (m, $COCH_3$). ^1H NMR: ($CDCl_3$) 5.72 (d of d, 1 H, Cp), 5.68 (d of d, 1 H, Cp), 5.54 (d of d, 1 H, Cp), 5.49 (d of d, 1 H, Cp), 5.39 (d of d, 1 H, Cp), 5.32 (d of d, 1 H, Cp), 2.44 (s, 3 H, $COCH_3$), 2.43 (s, 3 H, $COCH_3$), 2.40 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3). ^{13}C NMR: ($CDCl_3$) 95.1 (Cp), 94.8 (Cp), 91.6 (Cp), 91.4 (Cp), 90.4 (Cp), 90.0 (Cp), 29.7 ($COCH_3$), 14.9 (CH_3) (metal carbonyl, acyl and *ipso* carbons were not located).

A sample of **7** which was stored at room temperature for four weeks was chromatographed on alumina. After removal of **7** using dichloromethane, neat ethyl acetate eluted a small quantity of the purple tetranuclear complex, **9**. IR: ($CDCl_3$) 1690 (sh), 1675 (m). No trimer, **8**, was observed during the workup of this sample.

Synthesis of 1-acetyl, 2-methylcyclopentadienylrhodiumcarbonyl trinuclear complex, 8

6, 50 mg (0.18 mmol) and an excess of trimethylamine oxide, 0.1 g (1.33 mmol) were taken up in benzene and refluxed for two days. Upon removal of the solvent, the reaction mixture was eluted on alumina. Elution with dichloromethane yielded a pale yellow band which was found by IR to have no metal carbonyl bands and was not further investigated. Elution with ethyl acetate yielded a broad green band. Removal of solvent gave about 10 mg of **8** as a dark green solid. Yield 22%. IR: ($CDCl_3$) 1866 (s), 1819 (m), 1669 (m, $COCH_3$). ^1H NMR: ($CDCl_3$) 5.83 (broad s, 1 H, Cp), 5.79 (broad s, 1 H, Cp), 5.68 (broad s, 1 H, Cp), 5.62 (m, 2 H, Cp), 5.59 (m, 2 H, Cp), 5.50 (m, 3 H, Cp), 5.39 (t, 1 H, Cp), 5.35 (t, 1 H, Cp), 2.49 (s, 3 H, $COCH_3$), 2.47 (s, 1 H, $COCH_3$), 1.94 (s, 1 H, CH_3), 1.93 (s, 1 H, CH_3), 1.90 (s, 1 H, CH_3), 1.89 (s, 1 H, CH_3). ^{13}C NMR: ($CDCl_3$) 194.0 ($COCH_3$), 193.3 ($COCH_3$), 193.2 ($COCH_3$), 111.4 (*ipso* Cp), 110.8 (*ipso* Cp), 97.8 (d, Cp), 97.3 (s, Cp), 96.6 (d, Cp), 96.1 (d, Cp), 94.0 (d, Cp), 93.9 (d, Cp), 93.6 (d, Cp), 93.3 (s, Cp), 92.5 (d, Cp), 92.2 (d, Cp), 91.6 (s, Cp), 91.3 (d, Cp) (all ring carbon doublets had $J(Rh–C) \approx 3$ Hz), 43.4 ($COCH_3$), 28.3 ($COCH_3$), 28.2 ($COCH_3$), 22.3 ($COCH_3$), 14.5 (CH_3), 14.2 (CH_3), 14.1 (CH_3), 14.0 (CH_3).

1-acetyl, 3-methylcyclopentadienylrhodiumdicarbonyl, 7

A sample of **4** which was contaminated with **3** was used for the synthesis of **7**. $[ClRh(CO)_2]_2$ (0.50 g, 1.29 mmol) was allowed to react with a mixture of **4** and **3** (0.50 g, 1.54 mmol) in refluxing benzene as described above. Column chromatography of the resulting red oil on alumina with 20% dichloromethane in petroleum ether yielded two yellow-brown bands. The first band was shown by IR and ^1H NMR to be identical to **6** previously described. After solvent removal, the second band yielded 70 mg of **7** as a dark red oil. Yield: 16%. IR: (CH_2Cl_2) 2051 (s, Rh–CO), 1989 (s, Rh–CO), 1664 (m, $COCH_3$). ^1H NMR: ($CDCl_3$) 5.84 (1 H, t),

5.64 (1 H, t), 5.61 (1 H, m), 2.29 (s, 3 H), 2.11 (s, 3 H). ^{13}C NMR: ($CDCl_3$) 191.4 ($COCH_3$), 189.0 (Rh–CO, J(Rh–C) = 83.4 Hz), 111.0 (*ipso* Cp), 105.9 (*ipso* Cp), 93.8 (Cp, J(Rh–C) = 3.2 Hz), 87.9 (Cp, J(Rh–C) = 3.1 Hz), 84.4 (Cp, J(Rh–C) = 3.3 Hz), 26.1 ($COCH_3$), 14.2 (CH_3). Mass spectroscopy: (EI) 280 (49.9, M^+), 252 (78.9, $M^+ - CO$), 224 (100.0, $M^+ - 2$ CO), 222 (14.7, $M^+ - CO$ and CH_2O), 196 (21.8, $M^+ - 3$ CO), 194 (73.2, $M^+ - 2$ CO and CH_2O), 181 (48.8, $RhC_6H_6^+$). Chiral HPLC: (0.5 mL/min) no observed resolution.

Synthesis of 1-acetyl, 2-methylcyclopentadienylrhodium(carbonyl)triphenylphosphine, ***11***

6 (0.70 g, 2.5 mmol) and triphenylphosphine (0.70 g, 2.7 mmol) were taken up in benzene and refluxed under nitrogen for two days. The resulting oil, which is insoluble in benzene, was triturated with 10% THF in hexane to give 1.22 g of **11** as a brick red solid. Yield: 95%. Mp 114–115°C. IR: (CH_2Cl_2) 1957 (s, Rh–CO), 1641 (m, $COCH_3$). ^{1}H NMR: ($CDCl_3$) 7.53–7.36 (mult., 15 H, PPh_3), 5.52 (broad s, 1 H, H-4), 5.16 (d of d, J = 0.88 and 2.84 Hz, 1 H, H-3), 4.64 (d of d, J = 1.97 and 2.85 Hz, 1 H, H-5), 2.12 (d, J = 4.07 Hz, 3 H, Cp–CH_3), 2.05 (s, 3 H, CO–CH_3). ^{13}C NMR: 193.5 (Rh–CO, J(Rh–C) = 86.9 Hz, J(P–C) = 23.4 Hz), 192.5 (*CO*), 135.9 (*ipso* Ph, J(P–C) = 47.3 Hz), 133.7 (*ortho* Ph, J(P–C) = 12.5 Hz), 130.1 (*para* Ph), 128.2 (*meta* Ph, J(P–C) = 10.2 Hz), 104.5 (*ipso* Cp–CH_3), 98.3 (*ipso* Cp–$COCH_3$), 95.0 (Cp), 89.4 (Cp), 88.3 (Cp), 27.2 ($COCH_3$), 14.7 (CH_3). ^{31}P NMR: ($CDCl_3$) 50.04 (J(Rh–P) = 197.0 Hz). Mass spectroscopy: (EI) 514 (15.7, M^+), 486 (100.0, $M^+ - CO$), 443 (23.1, $M^+ - CO$ and $COCH_3$), 286 (39.8, unk), 262 (16.0, PPh_3). Chiral HPLC: (0.5 mL/min) $t_{R1'}$ = 9.9 min, $t_{R2'}$ = 21.4 min, α = 2.17. Analysis. Found: C, 62.92; H, 4.85. $C_{27}H_{24}O_2PRh$ calc.: C, 63.04; H, 4.67%.

Synthesis of diastereomeric mixture of 1-acetyl, 2-methylcyclopentadienylrhodium (acetyl)(iodo)triphenylphosphine, ***12***

11 (250 mg, 0.49 mmol) was taken up in dichloromethane (10 mL) and an excess of iodomethane (4.56 g, 32 mmol) was added in one portion. The color of the reaction mixture darkened rapidly. After 2 h at room temperature, the solvents were removed to give a brown solid. Recrystallization from dichloromethane/octane gave **12** as a black crystalline solid in quantitative yield. Mp: 159–160°C. IR: (CH_2Cl_2) 1675 (m), 1663 (m). ^{1}H NMR: ($CDCl_3$) Major isomer: 7.52–7.40 (m, 15 H, PPh_3), 6.09 (m, 1 H, Cp), 5.08 (m, 1 H, Cp), 4.64 (t, 1 H, Cp), 2.77 (s, 3 H, Rh–$COCH_3$), 2.51 (s, 3 H, $COCH_3$), 1.63 (d, 3 H, J(P–H) = 4.07 Hz, CH_3). Minor isomer: 7.52–7.40 (m, 15 H, PPh_3), 5.39 (t, 1 H, Cp), 4.88 (d, 1 H, Cp), 4.78 (t, 1 H, Cp), 2.90 (s, 3 H, Rh–$COCH_3$), 2.52 (d, 3 H, J(P–H) = 4.07 Hz, CH_3), 2.19 (s, 3 H, $COCH_3$). ^{13}C NMR: ($CDCl_3$) Major isomer: 231.6 (d of d, J(P–C) = 10.7 Hz, J(Rh–C) = 25.4 Hz, Rh–$COCH_3$), 194.9 (s, Cp–$COCH_3$), 134.3 (broad t, *ortho* Ph), 132.7 (d, J(2P–C) = 50.9, *ipso* Ph), 130.7 (d of d, $J \approx 2$ Hz, *para* Ph), 128.1 (d of d, J = 10.5 Hz, $J \approx 1$ Hz, *meta* Ph), 123.4 (s, *ipso* Cp), 100.8 (s, *ipso* Cp), 94.4 (d of d, J = 3.6 Hz, J = 8.0 Hz, Cp), 93.9 (d of d, $J \approx 2$ Hz, Cp), 91.3 (d, J = 4.9 Hz, Cp), 54.0 (s, Rh–$COCH_3$), 29.9 (s, Cp–$COCH_3$), 13.9 (s, Cp–CH_3). Minor isomer: 232.3 (d of d, J(P–C) = 9.7 Hz, J(Rh–C) = 25.3 Hz, Rh–$COCH_3$), 194.1 (s, Cp–$COCH_3$), 134.3 (broad t, *ortho* Ph), 132.7 (d, J(2P–C) = 50.9, *ipso* Ph), 130.7 (d of d, $J \approx 2$ Hz, *para* Ph), 128.1 (d of d, J = 10.5 Hz, $J \approx 1$ Hz, *meta* Ph),

Table 1

Crystallographic data for **11**

(a) Crystal parameters			
Formula	$C_{27}H_{24}O_2PRh$	V, Å^3	2354.7(7)
Formula weight	514.37	Z	4
Crystal system	monoclinic	crystal dimensions, mm	0.20×0.30×0.40
Space group	$P2_1/c$	crystal color	orange
a, Å	9.029(1)	D_{calc}, g cm^3	1.451
b, Å	11.196(2)	μ(Mo-K_α), cm^{-1}	7.87
c, Å	23.298(4)	Temperature, K	297
β, deg	91.34(1)		
(b) Data collection			
Diffractometer	Nicolet	Reflections collected	5844
Monochromator	Graphite	Independent reflections	5428
Radiation	Mo-K_α (λ = 0.71073 Å)	Independent observed reflections $F_o \leqslant n\sigma(F_o)$ (n = 4)	4083
2θ scan range, deg	4–55	Standard reflections	3 stds/197 rflns
Data collected	$\pm h$, $+k$, $+l$	Variation in standards	<1
(c) Refinement			
$R(F)$, %	3.65	$\Delta(\rho)$, e Å^{-3}	0.73
$R(wF)$, %	4.06	N_o/N_v	15.9
Δ/σ(max)	0.04	GOF	1.070

118.3 (d, J = 3 Hz, *ipso* Cp), 101.0 (s, *ipso* Cp), 100.3 (s, Cp), 94.9 (d of d, $J \approx$ 4.8 Hz, Cp), 87.4 (d, J = 5.0 Hz, Cp), 54.7 (s, Rh–COCH_3), 29.8 (s, Cp–COCH_3), 15.8 (s, Cp–CH_3). ^{31}P NMR: ($CDCl_3$) Major isomer: 40.67 (J(Rh–P) = 168.1 Hz); minor isomer: 39.13 (J(Rh–P) = 165.5 Hz). Chiral HPLC: (0.5 mL/min) Major isomer: $t_{R1'}$ = 28.5 min, $t_{R2'}$ = 48.0 min, α = 1.68. Minor isomer: $t_{R1'}$ = 33.6 min, $t_{R2'}$ = 36.9 min, α = 1.10. Analysis. Found: C, 51.22; H, 4.10. $C_{28}H_{27}O_2IPRh$ calc.: C, 51.24; H, 4.12%.

Crystal structure determination for 11

Data relating to the crystal parameters and the data collection parameters for **11** are collected in Table 1. Crystals were mounted in epoxy cement on a fine glass fiber. Photographic evidence established $2/m$ Laue symmetry, and systematic absences in the diffraction data allowed a unique assignment of the space group. No correction for absorption was required (the max/min transmission ratio was less than 1.1).

The structure was solved by locating the Rh atom from a Patterson map, and was completed from subsequent difference Fourier syntheses. Hydrogen atoms of the two methyl groups were found and isotropically refined owing to the absence of a rotational reference. Other hydrogen atoms were idealized. All non-hydrogen atoms were anisotropically refined. The phenyl rings were constrained to rigid, regular hexagons.

All calculations used the SHELXTL program library (version 5.1) (G.M. Sheldrick, Nicolet (Siemens), Madison, WI). Atomic coordinates are given in Table 2 and selected bond distances and angles in Table 3.

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for **11**

	x	*y*	*z*	*U* [a]
Rh	2660.9(3)	994.7(2)	1351.8(1)	36.6(1)
P	1697.7(9)	2423.2(8)	765.9(4)	36.9(2)
O(6)	46(4)	−1005(3)	2385(1)	68(1)
O(9)	2971(5)	−787(3)	412(2)	89(1)
C(1)	1821(4)	512(3)	2255(1)	42(1)
C(2)	3086(4)	−193(4)	2126(2)	51(1)
C(3)	4321(4)	609(4)	2085(2)	59(1)
C(4)	3821(4)	1777(4)	2155(2)	60(1)
C(5)	2256(4)	1737(3)	2240(1)	46(1)
C(6)	319(4)	67(3)	2356(1)	47(1)
C(7)	−884(5)	969(4)	2429(2)	74(2)
C(8)	3198(6)	−1529(4)	2103(2)	67(2)
C(9)	2834(5)	−62(4)	758(2)	57(1)
C(11)	489(2)	2327(3)	−368(1)	74(2)
C(12)	576	2125	−958	96(2)
C(13)	1901	1732	−1189	90(2)
C(14)	3139	1540	−831	71(2)
C(15)	3052	1742	−242	56(1)
C(16)	1727	2135	−11	44(1)
C(21)	2977(3)	4357(2)	1358(1)	58(1)
C(22)	3630	5483	1408	69(2)
C(23)	3850	6173	919	82(2)
C(24)	3419	5738	380	113(3)
C(25)	2766	4613	329	85(2)
C(26)	2545	3922	818	41(1)
C(31)	−1234(3)	1751(2)	868(1)	62(1)
C(32)	−2732	1912	980	80(2)
C(33)	−3257	3038	1131	82(2)
C(34)	−2283	4004	1171	86(2)
C(35)	−785	3843	1059	64(2)
C(36)	−261	2717	908	45(1)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Bond distances (Å) and angles (deg) for **11**

(a) Bond distances			
Rh–CNT	1.940(3)	Rh–C(9)	1.829(4)
Rh–P	2.263(1)	C(9)–O(9)	1.153(5)
(b) Bond angles			
Rh–C(9)–O(9)	175.3(4)	CNT–Rh–C(9)	133.5(2)
CNT–Rh–P	134.2(1)	C(9)–Rh–P	92.3(1)

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