

that attached to the  $\pi$ -ring system and especially when it meets stereochemically desirable environments, such as the present octahedral MO<sub>4</sub> rigid core.

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## Structure of the Rhodium Complex of a Reactant in Directed Hydrogenation

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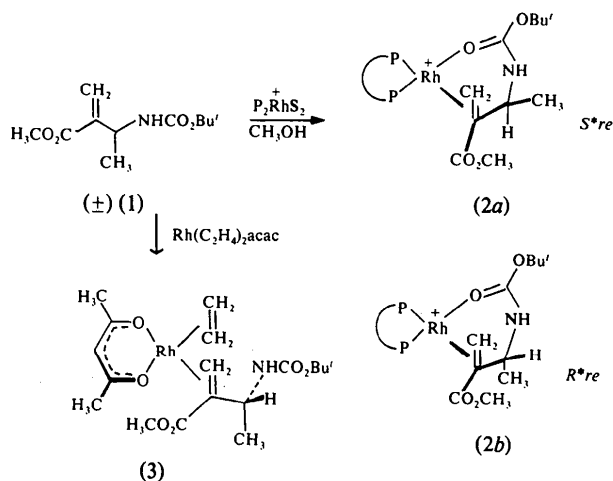
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**Abstract.**  $\{\eta^2\text{-}[2R^*(re),3R^*]\text{-}3\text{-}(tert\text{-Butoxycarbonyl-amino})\text{-}2\text{-methoxycarbonylbut-1-ene}\}(\eta^2\text{-ethene})(2,4\text{-pentanedionato})\text{rhodium}$ , [Rh(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)(C<sub>2</sub>H<sub>4</sub>)(C<sub>11</sub>H<sub>19</sub>NO<sub>4</sub>)],  $M_r = 459.35$ , monoclinic,  $P2_1/n$ ,  $a = 12.547$  (3),  $b = 9.021$  (2),  $c = 18.869$  (5) Å,  $\beta = 105.68$  (2)°,  $V = 2056.2$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.48$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 8.42$  cm<sup>-1</sup>,  $F(000) = 952$ ,  $T = 290$  K,  $R = 0.046$  for 2384 unique observed [ $I/\sigma(I) \geq 2.0$ ] reflections. The potentially chelating ligand is only bound to Rh through its olefin group, in  $R$  re conformation (and its  $S$  si enantiomer). Rh–C is 2.13 (1) Å, Rh–O is 2.036 (3) Å and C–C(olefin) 1.38 (1) Å.

**Introduction.** The directed hydrogenation of  $\alpha'$ -substituted acrylate esters can lead to high stereoselectivity (Brown, 1987) and, with an optically active ligand coordinated to the catalytic metal centre, kinetic resolution of racemic starting material can occur. This leads to catalytic asymmetric synthesis of a range of saturated and unsaturated esters (Brown & Cutting, 1985; Brown & James, 1987; Brown, James & Prior, 1987). Selectivity arises through the coordination of both olefin and directing group to rhodium during key stages of the catalytic cycle. There is a lack of appropriate structural information on the chelate binding of reactants such as (1). The chiral centre adjacent to the olefin requires that two configurational isomers of coordi-

nated catalytic intermediates exist; these are schematized as (2a) and (2b). Catalytic hydrogenation studies suggest that complexes of type (2a) are favoured in the stereochemically determining step of the catalytic cycle.



Several attempts have been made to clarify these stereochemical requirements, but difficulty has been found in preparing crystalline samples suitable for X-ray characterization. In the course of this work the unsaturated amide (1) (Brown & James, 1987) was reacted with bis(ethylene)rhodium acetylacetonate, with the displacement of one molecule of ethylene. The complex (3) produced provides an analogue of (2a–b),

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Table 1. Atom coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

|       | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> |
|-------|------------|------------|------------|----------|
| Rh    | 4257.6 (4) | 1043.1 (5) | 1331.7 (3) | 35 (1)*  |
| O(1)  | 5902 (3)   | 912 (5)    | 1867 (2)   | 48 (2)*  |
| O(2)  | 4372 (3)   | -869 (4)   | 788 (2)    | 50 (2)*  |
| O(3)  | 5378 (3)   | -803 (4)   | 3987 (2)   | 44 (1)*  |
| O(4)  | 6642 (3)   | 885 (5)    | 3813 (2)   | 54 (2)*  |
| O(5)  | 2621 (3)   | 2173 (4)   | 2639 (2)   | 43 (2)*  |
| O(6)  | 2305 (3)   | 3826 (5)   | 1730 (2)   | 51 (2)*  |
| N(1)  | 4815 (3)   | 1027 (6)   | 3219 (3)   | 37 (2)*  |
| H(N1) | 4263 (46)  | 826 (81)   | 3244 (34)  | 70       |
| C(1)  | 7655 (5)   | -63 (8)    | 2373 (4)   | 62 (3)*  |
| C(2)  | 6537 (5)   | -178 (7)   | 1831 (4)   | 50 (3)*  |
| C(3)  | 6261 (5)   | -1382 (7)  | 1375 (4)   | 54 (3)*  |
| C(4)  | 5241 (6)   | -1670 (7)  | 878 (4)    | 52 (3)*  |
| C(5)  | 5103 (6)   | -3017 (8)  | 403 (4)    | 74 (4)*  |
| C(6)  | 6777 (5)   | -906 (8)   | 5174 (3)   | 58 (3)*  |
| C(7)  | 5422 (5)   | -2895 (7)  | 4697 (4)   | 60 (3)*  |
| C(8)  | 6931 (6)   | -2467 (8)  | 4104 (4)   | 70 (3)*  |
| C(9)  | 6172 (4)   | -1748 (6)  | 4500 (3)   | 39 (2)*  |
| C(10) | 5704 (5)   | 410 (6)    | 3689 (3)   | 36 (2)*  |
| C(11) | 4922 (4)   | 2452 (7)   | 2877 (3)   | 32 (2)*  |
| C(12) | 4911 (5)   | 3753 (7)   | 3387 (3)   | 46 (2)*  |
| C(13) | 4098 (4)   | 2670 (6)   | 2127 (3)   | 32 (2)*  |
| C(14) | 4426 (4)   | 3320 (7)   | 1547 (3)   | 38 (2)*  |
| C(15) | 2920 (4)   | 2980 (6)   | 2128 (3)   | 36 (2)*  |
| C(16) | 1502 (4)   | 2382 (8)   | 2690 (4)   | 52 (3)*  |
| C(17) | 2532 (5)   | 585 (8)    | 976 (4)    | 49 (3)*  |
| C(18) | 2789 (5)   | 1466 (7)   | 462 (3)    | 54 (3)*  |

\* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

|                |           |                   |            |
|----------------|-----------|-------------------|------------|
| Rh—O(1)        | 2.041 (3) | Rh—C(17)          | 2.127 (6)  |
| Rh—O(2)        | 2.031 (4) | Rh—C(18)          | 2.144 (5)  |
| Rh—C(13)       | 2.146 (6) | C(13)—C(14)       | 1.398 (8)  |
| Rh—C(14)       | 2.094 (6) | C(17)—C(18)       | 1.358 (10) |
| O(1)—Rh—O(2)   | 90.1 (2)  | C(17)—Rh—C(18)    | 37.1 (3)   |
| C(13)—Rh—C(14) | 38.5 (2)  | C(11)—C(13)—C(15) | 116.3 (5)  |

with the phosphine ligand replaced by the diketonate, but with the amide (1) coordinated only through its olefin group.

**Experimental.** The racemic amide (1) [3-(*tert*-butoxycarbonylamino)-2-methoxycarbonylbut-1-ene; 0.12 g, 0.5 mmol] was added in one portion to a stirred solution of bis(ethylene)(2,4-pentanedionato)rhodium (0.13 g, 0.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (4 ml) under Ar. After 30 min the colour changed from yellow to orange, and evolution of ethylene was observed. Stirring was continued overnight, solvent removed *in vacuo* and the orange powder washed with hexane, pre-cooled to 273 K. The product had *m/z* 431 and was presumed to be a diastereomeric mixture. This was recrystallized by dissolution in a small quantity of  $\text{CH}_2\text{Cl}_2$ ; addition of a layer of hexane which was permitted to diffuse slowly into the solution gave crystals suitable for X-ray analysis. Crystal character: orange hexagonal plates. Data were collected from  $\omega/2\theta$  scans with a Syntex P2<sub>1</sub> four-circle diffractometer. Maximum  $2\theta$  was  $50^\circ$ , with scan range  $\pm 1.1^\circ$  ( $2\theta$ ) around the  $K\alpha_1$ – $K\alpha_2$  angles,

scan speed  $3$ – $29^\circ \text{ min}^{-1}$ , depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. *hkl* ranges were: 0/14; 0/10;  $-22/21$ . Three standard reflections were monitored every 200 reflections, and showed negligible changes during data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ( $18 \leq 2\theta \leq 20^\circ$ ). Reflections were processed using profile analysis to give 3627 unique reflections ( $R_{\text{int}} = 0.032$ ); 2384 were considered observed [ $I/\sigma(I) \geq 2.0$ ] and used in refinement; they were corrected for Lorentz, polarization and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.93 and 0.90. Crystal dimensions were  $0.19 \times 0.18 \times 0.08 \text{ mm}$ , with bounding faces  $\{110\}$ ,  $\pm(101)$ ,  $\{001\}$ . Systematic absences:  $h0l$ ,  $h+l \neq 2n$ ;  $0k0$ ,  $k \neq 2n$ . Heavy atoms were located by the Patterson interpretation section of *SHELXTL* (Sheldrick, 1983) and the light atoms then

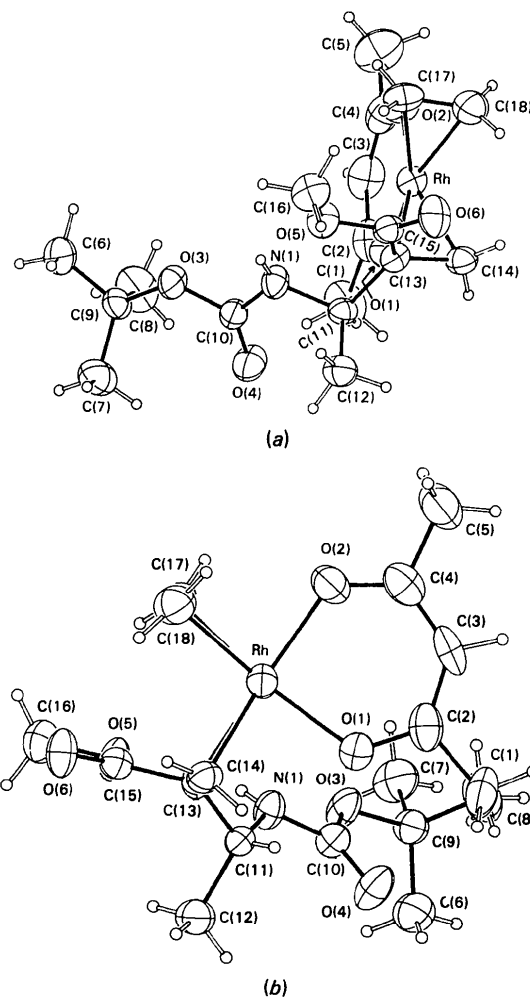


Fig. 1. View of the complex, (a) parallel to the Rh coordination plane, showing the atomic numbering, (b) perpendicular to the coordination plane, showing the relative conformations.

found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. H atoms were given fixed isotropic temperature factors,  $U = 0.07 \text{ \AA}^2$ . All were visible on difference Fourier syntheses, but proved slightly unstable on refinement. A weak C–H constraint [0.94 (2) Å] was applied to H atoms attached to C(14), C(17) and C(18), those nearest the metal atom and likely to be most affected by diffraction ripples. These atoms then refined to chemically satisfactory positions. Methyl groups were treated as rigid CH<sub>3</sub> units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Final refinement was on  $F$  by cascaded least-squares methods refining 283 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height 0.7 and  $-0.6 \text{ e \AA}^{-3}$ . A weighting scheme of the form  $w = 1/(\sigma^2 F + gF^2)$  with  $g = 0.00013$  was used and shown to be satisfactory by a weight analysis. Final  $R = 0.046$ ,  $wR = 0.039$ . Maximum shift/e.s.d. in final cycle 0.4. Computing was with *SHELXTL* on a Data General DG30. Scattering factors in the analytical form and anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1, and selected bond lengths and angles in Table 2.\*

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51540 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** Figs. 1(a) and 1(b) show views of the complex parallel and perpendicular to the Rh coordination plane respectively. The molecular configuration is more obvious from Fig. 1(b). The unit cell is a racemate of this form and its enantiomer. Thus only one of the two possible configurational isomers of the coordinated amide, with *R re* relative configuration is observed. This corresponds to the stereoisomer which would be disfavoured on the directed hydrogenation pathway and it is notable that the amide remains uncoordinated. The torsion angle which defines steric interactions around the coordinated olefin is  $\text{H}_3\text{C}-\text{C}-\text{C}_\alpha-\text{CO}_2\text{Me}$ . In the crystal this is  $-54.4 (5)^\circ$  but inspection of molecular models indicates that chelate coordination of the amide carbonyl group would alter this to around  $0^\circ$  and entail severe eclipsing interactions between the CH<sub>3</sub> and ester group (*cf.* 2b).

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## The Structure of $[\text{Co}_4(\text{CO})_8(\mu_4\text{-PPh})_2\{\text{P}(\text{OEt})_3\}_2]$ . Further Evidence for Thermodynamic Product Control in Ligand Substitution Reactions Involving $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$

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**Abstract.** Di- $\mu$ -carbonyl-hexacarbonyl-bis( $\mu_4$ -diphenylphosphindene)-bis(triethoxyphosphine)tetracobalt(I)-

(4Co–Co),  $[\text{Co}_4(\text{CO})_8(\text{C}_6\text{H}_5\text{P})_2\{\text{P}(\text{C}_2\text{H}_5\text{O})_3\}_2]$ ,  $M_r = 1008.29$ , monoclinic,  $P2_1/n$ ,  $a = 10.348 (1)$ ,  $b = 17.186 (2)$ ,  $c = 12.311 (1) \text{ \AA}$ ,  $\beta = 106.07 (1)^\circ$ ,  $V = 2103.7 (4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.592 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 17.56 \text{ cm}^{-1}$ ,  $F(000) = 1024$ ,  $T = 293 \text{ K}$ ,  $R = 0.0349$  for 3209 independent reflections.

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