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Asymmetric Hydrosilation of Ketones, Catalyzed by Rhodium Complexes Containing Chiral Chelate Ligands. Crystal and Molecular Structure of (Bicyclo[2.2.1]hepta-2,5-diene)[(*S*)-*N*,*N*-dimethyl-1-(*o*-(diphenylarsino)phenyl)ethylamine]rhodium(I) Perchlorate

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Two chiral, bidentate ligands of formula *o*-(X(C_6H_5)$_2$)C_6H_4CH(CH_3)N(CH_3)$_2$, amphos (X = phosphorus) and amars (X = arsenic), have been prepared in good yield from (*R*)- and (*S*)-1-phenylethylamine. Rhodium complexes of these ligands have been used for the asymmetric hydrosilation of a series of prochiral ketones. For comparison purposes, the reactions were repeated with Rh catalysts containing the chiral, diphosphine species (*S*,*S*)-chiraphos and (+)-diop. The maximum enantiomeric excess of 72% was achieved with the amphos catalyst, while, in contrast, the amars catalyst gave no induction. An explanation for this behavior is proposed, on the basis of the results of a three-dimensional single-crystal X-ray study of [Rh(*S*-amars)(C_7H_8)]ClO_4. The salt crystallizes in space group *P*1 with two formula units per cell and unit cell dimensions a = 10.154 (6) Å, b = 15.082 (9) Å, c = 9.538 (6) Å, α = 97.64 (1)°, β = 96.05 (1)°, and γ = 74.43 (1)°. The structure has been refined by full-matrix least-squares techniques on F, with the use of 3834 reflections with $I > 3\sigma(I)$, to a final agreement factor of R_1 = 0.059. The two independent chiral cations have essentially square-planar coordination geometries at the Rh atoms (if the diene is viewed as a bidentate chelating ligand), with average Rh–As and Rh–N distances of 2.398 (3) and 2.177 (18) Å, respectively. Each six-membered ring adopts a λ-twist boat conformation. In spite of this, enantiotopic dispositions of the pseudo axial–equatorial arrangements of the phenyl rings are observed in the unit cell, a conformational flexibility which is presumably responsible for the observed optical yields.

Introduction

The modification of Wilkinson-type catalysts for asymmetric synthesis has received considerable attention of late, with the major thrust of the research being the development of catalysts for the asymmetric hydrogenation of amino acid precursors.[2-6] The hydrosilation of prochiral ketones to give chiral silyl ethers has been investigated to a lesser extent, and in general catalysts incorporating chiral diphosphines have been used for these purposes.[7-9]

As part of our continuing interest in this subject,[10,11] we have addressed two of the major difficulties encountered in these studies: the convenient preparation in good yields of the chiral chelate ligands required for the catalyst complex and the development of an understanding of how structural modifications to the chiral ligands affect the optical yields.

We describe herein the facile preparation in high yields of two chiral ligands, an aminoarsine, amars (**1**), and its aminophosphine analogue, amphos (**2**). The Rh catalysts containing these and other bidentate phosphine ligands have been used to study the hydrosilation of a number of prochiral ketones. Variations in ligand structure greatly affect the optical yields, with essentially no asymmetric induction by the amars catalyst. An explanation for this observation is proposed, based upon the results of a single-crystal X-ray structure determination of [Rh(*S*-amars)(C_7H_8)]ClO_4 described below.

Experimental Section

The preparations and hydrosilations were carried out under an atmosphere of dry, O_2-free N_2. ^1H and ^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer using $Si(CH_3)_4$ and $OP(OCH_3)_3$ as the respective references. Melting points are reported uncorrected. All rotations refer to the sodium D line and were recorded with a Jasco optical rotary dispersion recorder, Model ORD/UV-5. Combustion analyses were performed by Guelph Chemical Lab., Guelph, Ontario, Canada. $RhCl_3 \cdot xH_2O$ was purchased from Johnson-Matthey Ltd. $(+)_{589}$-2,3-*O*-isopropylidenedioxy-1,4-bis(diphenylphosphino)butane ((+)-diop) was purchased from the Strem Chemical Co. (2*S*,3*S*)-bis(diphenylphosphino)butane (*S*,*S*-chiraphos) was prepared by a minor modification of the published route.[4,11]

Preparation of (*S*)-*o*-(As(C_6H_5)$_2$)C_6H_4CH(CH_3)N(CH_3)$_2$·HCl (*S*-amars·HCl). (*S*)-*N*,*N*-Dimethyl-1-phenylethylamine was prepared from (*S*)-1-phenylethylamine by reaction with formaldehyde and formic acid.[12] (*S*)-*N*,*N*-Dimethyl-1-phenylethylamine (5.73 g) was dissolved in dry, freshly distilled diethyl ether (30 mL), and 15.7 mL of BuLi in hexane (2.45 M) was added. The mixture was stirred for 24 h and cooled to 0 °C and As(C_6H_5)$_2$Cl (10 g) was added slowly. The mixture was stirred for 4 h, after which H_2O (100 mL) was added with cooling. The organic layer was separated and the aqueous phase extracted with ether (2 × 50 mL). The combined organic phases were treated with aqueous HCl and then cooled. The white precipitate was collected and washed with H_2O and ether. Recrystallization from CH_2Cl_2/ether gave 5.0 g (31%) of product: $[\alpha]^{25}_D$ = +34.9° (CH_2Cl_2, *c* 8.2, *l* 0.1); mp 205–210 °C dec. Anal. Calcd for $C_{22}H_{25}AsClN$: C, 63.85; H, 6.09. Found: C, 63.14; H, 6.11.

Preparation of (*S*)-*o*-(As(C_6H_5)$_2$)C_6H_4CH(CH_3)N(CH_3)$_2$ (*S*-amars, 1). *S*-amars·HCl (1 g) was shaken with excess NaOH in ethanol for 10 min. After centrifugation, the solvent was removed, the residue taken up in diethyl ether and filtered, the solvent removed once again, and the resulting solid recrystallized from ethanol/methanol: $[\alpha]^{25}_D$ = −22.3° (CH_2Cl_2, *c* 6.6, *l* 0.1); mp 53–55 °C. Anal. Calcd for $C_{22}H_{24}AsN$: C, 70.02; H, 6.41. Found: C, 69.91; H, 6.44.

Preparation of (*R*)-*o*-(P(C_6H_5)$_2$)C_6H_4CHCH$_3$N(CH_3)$_2$·HCl·(acetone) (*R*-amphos·HCl·(acetone)). (*R*)-*N*,*N*-Dimethyl-1-phenylethylamine (16.4 g) in diethyl ether (100 mL) was reacted with 44.9 mL of BuLi in hexane (2.45 M) as described above. P(C_6H_5)$_2$Cl (19.7 mL) was added slowly. The solution was stirred for 2 h, after which H_2O (75 mL) was added. The organic layer was separated and the aqueous phase extracted with ether (3 × 50 mL). The combined organic phase was dried ($MgSO_4$). The solution was filtered, HCl gas was passed through the solution, and *R*-amphos·HCl was collected. This crude product was recrystallized from hot acetone/ether to give 24.5 g (60%) of *R*-amphos·HCl·(acetone): $[\alpha]^{25}_D$ = −21.5°

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(CH_2Cl_2, *c* 8, *l* 0.1); $[\alpha]^{25}_D$ = −31.9° (EtOH, *c* 1.1, *l* 1); mp 205–206 °C dec. Anal. Calcd for $C_{25}H_{31}ClNOP$: C, 70.17; H, 7.30. Found: C, 70.06; H, 7.04.

In an analogous manner, *S*-amphos·HCl·(acetone) was prepared. $[\alpha]^{25}_D$ = +23.0° (CH_2Cl_2, *c* 8, *l* 0.1); mp 205–206 °C dec. Anal. Calcd for $C_{25}H_{31}ClNOP$: C, 70.17; H, 7.30. Found: C, 70.55; H, 7.18.

Preparation of (*R*)-*o*-($P(C_6H_5)_2$)$C_6H_4CH(CH_3)N(CH_3)_2$ (*R*-amphos, 1).[13] The procedure followed that used for *S*-amars. The crude product was crystallized from CH_3OH: $[\alpha]^{25}_D$ = +54.4° (CH_2Cl_2, *c* 8, *l* 0.1); mp 66–68 °C. Anal. Calcd for $C_{22}H_{24}NP$: C, 79.25; H, 7.26. Found: C, 79.86; H, 7.59.

S-amphos was obtained by a similar route: $[\alpha]^{25}_D$ = −52.3° (CH_2Cl_2, *c* 8, *l* 0.1); mp 66–68 °C. Anal. Calcd for $C_{22}H_{24}NP$: C, 79.25; H, 7.26. Found: C, 78.53; H, 7.30.

Preparation of [Rh(*S*-amars)C_7H_8]ClO_4. [Rh(C_7H_8)$_2$]ClO_4 and *S*-amars (95 mg) were dissolved in degassed CH_2Cl_2 (3 mL). Tetrahydrofuran was added slowly, followed by a few drops of hexane. The solution was filtered and allowed to stand overnight. A low yield of crystalline product was obtained; mp 160–165 °C dec. Anal. Calcd for $C_{29}H_{32}AsClNO_4Rh$: C, 51.84; H, 4.80. Found: C, 51.78; H, 5.06.

In a similar manner, [Rh(*S*-amphos)C_7H_8]ClO_4 was prepared and crystallized from CH_2Cl_2/diethyl ether; mp 170–180 °C dec. Anal. Calcd for $C_{29}H_{32}ClNO_4P$: C, 55.47; H, 5.30. Found: C, 55.47; H, 5.18.

Procedure for Hydrosilation of Ketones. The hydrosilations were all performed as described below for acetophenone, with the appropriate modifications.

[$RhCl(C_2H_4)_2]_2$[14] (20 mg) and *R*-amphos (35 mg) were dissolved in degassed benzene (10 mL). $(C_6H_5)_2SiH_2$ (6.0 mL) was added followed by acetophenone (3.45 mL). The mixture was stirred for 72 h. The completion of the reaction was checked by ^1H NMR spectroscopy. The benzene was removed by distillation and the silyl ether $(C_6H_5)CH(CH_3)OSi(C_6H_5)_2H$ distilled under vacuum (145 °C (1 mm)). Four grams of product was isolated. $[\alpha]^{25}_D$ = +17.7° (neat, *l* 0.05). This indicated a 33% enantiomeric excess based on published data.[7]

In all cases, optical yields were determined by comparison with literature data, except for $C_2H_5CHCH_3OSi(C_6H_5)_2H$, which was prepared as follows.

Preparation of (*R*)-$C_2H_5CHCH_3OSi(C_6H_5)_2H$. (*R*)-$C_2H_5CHCH_3OH$ (1.0 g) was dissolved in diethyl ether, 9.7 mL of MeLi in diethyl ether (1.4 M) was added, and the mixture was stirred for 2 h. $(C_6H_5)_2SiClH$[15] (2.82 g) in diethyl ether (10 mL) was added, the mixture was stirred for 2 h, and the product was obtained by fractional distillation under vacuum: $[\alpha]^{25}_D$ = −22.8° (neat, *l* 0.1).

Collection and Reduction of X-ray Data. Orange crystals of [Rh(*S*-amars)C_7H_8]ClO_4 were prepared as above. An extensive photographic examination employing Weissenberg and precession techniques showed the crystals were triclinic. The chiral nature of the complex led to an unambiguous assignment of the space group as *P*1, C_1^1, No. 1.[16]

A crystal approximately 0.20 × 0.25 × 0.25 mm of suitable quality was fractured from a clump. Six of the eight faces were readily identified as (01$\bar{1}$), (12$\bar{2}$), (100), ($\bar{1}$00), 010), and (0$\bar{1}$0). The two fractured faces were closely approximated by (150) and (314). After data collection, the crystal dimensions were accurately measured on a microscope fitted with a filar eyepiece to permit an absorption correction.

Intensity data were recorded on a Picker FACS-1 automatic diffractometer operating under the Vanderbilt system.[17] Cell constants and an orientation matrix were refined[18] with the use of 22 carefully centered reflections with 12° < 2θ < 24°. ω scans of several intense, low-angle reflections, recorded with a takeoff angle of 1.3° and a wide-open counter, had an average width at half-height of 0.17°. Full details of the experimental conditions are presented in Table I. During the collection of data, coincidence losses in counting were minimized by using attenuators, and five standard reflections were recorded every 200 reflections. A sharp decrease in intensity was observed during the time the first 500 reflections were collected. No crystal movement had occurred, and thereafter the standards showed only minor, random fluctuations. No correction was made for this variation. After data collection, ω scans of the standards showed no change in width at half-height, indicating no significant change in crystal mosaicity. A total of 6764 reflections (0 < 2θ < 55°) was measured. The data were corrected for monochromator polarization and Lorentz and polarization effects, and standard deviations based upon counting statistics were assigned.[19] There were 3834 reflections with $I > 3\sigma(I)$, and these were used in the solution and refinement of the structure.

Table I. Summary of Crystal Data and Experimental Conditions

compd	$C_{29}H_{32}AsClNO_4Rh$
mol wt	671.30
unit cell dimens	a = 10.154 (6) Å, b = 15.082 (9) Å, c = 9.538 (6) Å, α = 97.64 (1)°, β = 96.05 (1)°, γ = 74.43 (1)°
cell V	1390.8 Å^3
Z	2
density obsd	1.62 (1) g cm^{-3}
calcd	1.61 g cm^{-3}
space group	*P*1 (C_1^1, No. 1)
abs coeff	μ = 18.15 cm^{-1} for Mo Kα
radiation	Mo Kα, λ = 0.710 73 Å, graphite monochromatized
temp	22 °C
receiving aperture	5 × 5 mm, 32 cm from crystal
scan range	1.5° corrected for dispersion
bkgd	10 s stationary crystal, stationary counter at limits of scan
scan	θ–2θ at 2°/min
data collected	$+h, \pm k, \pm l$ for 0 ≤ 2θ < 55°
std reflctns	020, 110, 002, 1$\bar{1}$0, 011; recorded every 200 reflections

Solution and Refinement of the Structure. The solution was solved by the heavy-atom method and refined by full-matrix least-squares techniques on *F*. Scattering factors for neutral, nonhydrogen atoms were taken from ref 16b, while those for H were from Stewart, Davidson, and Simpson.[20] The real and imaginary anomalous dispersion corrections of Cromer and Liberman[21] were included for the Rh, As and Cl atoms. After the structure had been solved, the data were corrected for absorption effects by using the analytical method.[22] Transmission coefficients varied from 0.621 to 0.729.

Refinement was carried out by full-matrix least-squares techniques on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$, and F_o and F_c are the observed and calculated structure amplitudes. With 74 nonhydrogen and 64 H atoms per equivalent position, some constraints were required during refinement. The final, most satisfactory model involved group constraints[23] applied to six phenyl rings (D_{6h}; C–C = 1.392 Å), to the norbornadiene ligand,[24] and to the O_4 tetrahedra (T_d; Cl–O = 1.42 Å) of the perchlorate anions. The remaining Rh, Cl, As, N, and C atoms were assigned anisotropic thermal parameters. Individual isotropic thermal parameters were refined for the group atoms. H atom contributions were included in calculations of F_c, based upon idealized positions (sp^2 hybridization, C–H = 0.9 Å; sp^3 hybridization, C–H = 0.95 Å). All 64 H atoms were successfully located in difference Fourier syntheses. Isotropic Debye factors 10% greater than those of the atoms to which they are bonded were used, and, as the refinement progressed, all H atom parameters were recalculated. Since the absolute configuration of the ligand was known to be *S*, the correct

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Table II. Atomic Positional ($\times 10^4$) and Thermal Parameters ($\times 10^3$)

atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	0	0	0	49 (2)	42 (2)	49 (1)	−13 (1)	14 (1)	1 (1)
Rh(2)	4868 (2)	4858 (1)	4095 (2)	47 (2)	33 (1)	41 (1)	−7 (1)	11 (1)	5 (1)
As(1)	−2158 (3)	−54 (2)	730 (3)	36 (2)	39 (2)	50 (1)	−6 (1)	8 (1)	7 (1)
As(2)	7145 (3)	4907 (2)	3713 (3)	48 (2)	34 (2)	43 (1)	−6 (1)	5 (1)	6 (1)
Cl(1)	2665 (11)	−444 (6)	4971 (8)	192 (9)	53 (5)	90 (5)	−11 (6)	−75 (6)	−9 (4)
Cl(2)	2403 (7)	5368 (5)	−829 (7)	49 (4)	45 (4)	68 (4)	14 (3)	8 (3)	−2 (3)
N(1)	304 (20)	−1412 (13)	−1001 (20)	47 (13)	58 (13)	86 (15)	10 (10)	26 (12)	12 (12)
N(2)	4282 (18)	6365 (11)	4503 (18)	48 (12)	27 (9)	55 (12)	−2 (8)	4 (9)	12 (8)
C(17)	50 (24)	−2063 (12)	19 (24)	91 (19)	36 (12)	99 (19)	3 (12)	27 (16)	12 (13)
C(18)	827 (31)	−1924 (18)	1397 (23)	140 (26)	57 (19)	45 (13)	−9 (17)	−36 (16)	36 (13)
C(19)	1722 (30)	−1804 (19)	−1457 (25)	73 (20)	74 (18)	94 (18)	9 (14)	44 (15)	14 (14)
C(20)	−595 (25)	−1466 (19)	−2354 (23)	58 (17)	107 (22)	57 (15)	−44 (16)	20 (13)	22 (14)
C(47)	5242 (19)	6752 (13)	5380 (20)	36 (12)	45 (13)	65 (15)	0 (10)	−2 (11)	4 (11)
C(48)	5707 (33)	6203 (17)	6739 (23)	198 (29)	34 (14)	55 (15)	18 (17)	−21 (17)	−12 (11)
C(49)	2896 (29)	6696 (15)	5060 (24)	79 (19)	13 (11)	104 (19)	−15 (12)	33 (15)	−5 (11)
C(50)	4075 (22)	6730 (16)	3086 (27)	22 (13)	46 (16)	111 (20)	9 (12)	−9 (13)	−17 (14)

[a] $U_{ij} = \beta_{ij}/2\pi a_i^* a_j^*$ (Å^2). The form of the thermal ellipsoid is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$.

Table III. Group Parameters

group	x	y	z	δ[a]	ϵ	η
Ph(1)	−0.2767 (9)	−0.2098 (6)	0.0354 (7)	−0.223 (8)	−3.088 (7)	2.785 (7)
Ph(2)	−0.4699 (11)	0.1337 (7)	−0.0994 (9)	−2.199 (9)	−2.645 (8)	−0.648 (10)
Ph(3)	−0.2639 (11)	0.0595 (7)	0.4180 (9)	−1.519 (11)	−2.474 (8)	1.689 (10)
Ph(4)	0.7641 (9)	0.7022 (6)	0.4319 (7)	3.045 (7)	3.034 (7)	−2.639 (6)
Ph(5)	0.9706 (11)	0.3433 (8)	0.5311 (9)	0.884 (9)	2.735 (9)	−2.498 (10)
Ph(6)	0.7795 (10)	0.4365 (6)	0.0316 (9)	1.710 (10)	2.455 (7)	−1.657 (10)
ClO_4(1)	0.2802 (9)	−0.0459 (6)	0.4872 (9)	−0.608 (7)	2.934 (7)	0.862 (7)
ClO_4(2)	0.2615 (9)	0.5425 (6)	−0.0886 (9)	2.033 (7)	−3.039 (8)	−2.930 (6)
Nbd(1)	0.0876 (11)	0.0818 (7)	0.0272 (10)	2.625 (9)	−3.278 (9)	−2.696 (8)
Nbd(2)	0.4066 (10)	0.4041 (6)	0.3929 (9)	−0.472 (8)	−3.041 (8)	2.954 (7)

[a] x, y, and z are the fractional coordinates of the group origin; δ, ϵ, and η (radians) are the group orientation angles.[23]

choice of hand was made at the start. Under these conditions, after 3834 unique observations were employed and 260 variables refined, convergence was reached at values of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.059$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.038$. A statistical analysis of R_2 over various ranges of $|F_o|$, $\lambda^{-1}\sin\theta$, and diffractometer setting angles χ and ϕ showed no abnormal trends. The error in an observation of unit weight is 3.06 e. A total difference Fourier synthesis computed from structure factors based upon the final model showed no features of chemical significance. The two highest peaks, each of 1.04 (1) e Å^{-3}, at coordinates (0.272, −0.057, 0.500) and (−0.116, −0.003, 0.003), are of no chemical significance and are associated with Cl(1) and Rh(1), respectively.

So that the *S* absolute configuration could be confirmed, three cycles of refinement were performed on the inverted hand of the model, under the same conditions. Agreement factors of $R_1 = 0.073$ and $R_2 = 0.060$ were obtained, much poorer than those observed for the *S* model. Moreover, three C atoms had non-positive-definite temperature factors, and significantly different values were obtained for chemically equivalent bond lengths (e.g., Rh(1)–As(1) = 2.355 (5), Rh(2)–As(2) = 2.448 (5) Å). Accordingly, the *S* absolute configuration was deemed correct, and final positional and thermal parameters for this model are given in Table II for nongroup atoms. Group parameters are listed in Table III, while derived group atom values are given in Table IV. Hydrogen atom parameters (Table V) and structure amplitudes, as $10|F_o|$ and $10|F_c|$ in electrons, have been deposited.

Description of the Structure

The crystal is built up from unit cells each containing discrete cations and anions, as is evident from the shortest distances (Å) Rh(1)···Cl(1) = 5.237 (7), Rh(1)···Cl(2) = 6.72 (1), Rh(2)···Cl(2) = 5.134 (7), and Rh(1)···Rh(2) = 8.502 (4). The closest, nonbonded contacts between cations and anions are O(11)···H1C(23) = 2.46 and O(24)···H1C(73) = 2.53 Å, while contacts between cations and anions are all greater than H1C(18)···H1C(43) = 2.15 and H2C(18)···H3C(50) = 2.39 Å. In the absence of hydrogen bonding to the perchlorate anions, there may be some disorder present, as evidenced by the rather high thermal parameters, which range from 6.2 (3) to 16.4 (8) Å^2.

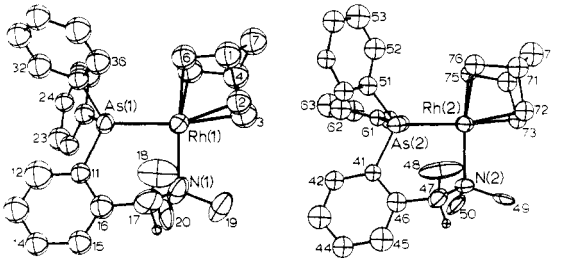

Figure 1. Perspective view of the cations, showing the atom numbering scheme; 50% probability thermal ellipsoids are drawn.

Selected interatomic dimensions are given in Table VI for the two cations; there is good agreement between chemically equivalent values. Perspective drawings of the cations showing the atom-numbering scheme are given Figure 1. The Rh atoms are coordinated in a square-planar geometry to the aminoarsine and the norbornadiene ligands. Fixed geometries were imposed upon the phenyl rings[23] and the diene ligand.[24] Other dimensions within the aminoarsine ligand are unexceptional.

The two six-membered chelate rings adopt twist-boat conformations of absolute configuration λ, and the configurations at C(17) and C(47) have been confirmed as *S*, as expected from the synthesis.[25,26] The amounts of twist are very similar, for C(17) is 1.10 (3) Å from the plane formed by Rh(1), As(1), and N(1), while C(47) is 0.89 (3) Å above the analogous plane in molecule 2. Whereas a lower energy conformer might have been predicted, in which the methyl substituents occupied equatorial positions, both C(18) and C(48) are axially disposed relative to the chelate ring. C(18) is 2.39 (2) and C(48) is 2.31 (3) Å from the respective planes formed by the

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Table IV. Derived Group Atom Parameters

atom	x^a	y	z	B, Å^2	atom	x	y	z	B, Å^2
				Ph(1)					
C(11)	−2451 (16)	−1248 (7)	457 (13)	3.4 (4)	C(14)	−3082 (13)	−2949 (7)	251 (12)	4.2 (4)
C(12)	−3743 (13)	−1287 (7)	765 (13)	6.9 (6)	C(15)	−1790 (11)	−2910 (7)	−57 (12)	4.5 (4)
C(13)	−4059 (10)	−2137 (10)	661 (12)	5.7 (5)	C(16)	−1474 (11)	−2059 (10)	47 (12)	4.5 (4)
				Ph(2)					
C(21)	−3685 (14)	742 (10)	−215 (15)	3.8 (5)	C(24)	−5714 (14)	1932 (9)	−1773 (13)	3.5 (5)
C(22)	−4483 (16)	382 (7)	−1304 (16)	3.5 (4)	C(25)	−4915 (17)	2291 (8)	−684 (15)	3.3 (5)
C(23)	−5498 (15)	977 (10)	−2082 (13)	5.0 (5)	C(26)	−3901 (15)	1696 (11)	94 (13)	4.1 (6)
				Ph(3)					
C(31)	−2432 (15)	350 (10)	2746 (10)	3.7 (4)	C(34)	−2846 (16)	840 (10)	5615 (10)	5.1 (5)
C(32)	−3758 (13)	676 (10)	3184 (13)	5.1 (5)	C(35)	−1520 (13)	514 (11)	5177 (13)	5.6 (6)
C(33)	−3965 (12)	921 (10)	4619 (14)	5.2 (5)	C(36)	−1313 (11)	269 (11)	3742 (15)	5.0 (6)
				Ph(4)					
C(41)	7504 (13)	6119 (6)	4151 (12)	2.6 (4)	C(44)	7779 (13)	7925 (6)	4487 (12)	4.2 (4)
C(42)	8657 (11)	6304 (7)	3706 (12)	3.5 (4)	C(45)	6626 (11)	7740 (7)	4932 (11)	5.4 (5)
C(43)	8794 (10)	7206 (9)	3874 (12)	5.2 (5)	C(46)	6489 (10)	6837 (9)	4764 (11)	3.8 (4)
				Ph(5)					
C(51)	8693 (13)	4098 (10)	4652 (14)	3.4 (5)	C(54)	10720 (15)	2768 (9)	5970 (15)	4.5 (5)
C(52)	8800 (16)	3162 (12)	4248 (14)	4.5 (6)	C(55)	10612 (13)	3705 (10)	6374 (12)	3.1 (4)
C(53)	9813 (18)	2497 (8)	4908 (16)	5.8 (7)	C(56)	9599 (15)	4370 (8)	5714 (15)	3.5 (4)
				Ph(6)					
C(61)	7554 (14)	4577 (9)	1747 (9)	2.6 (4)	C(64)	8036 (14)	4154 (9)	−1115 (9)	4.8 (5)
C(62)	6461 (10)	4590 (10)	731 (12)	2.6 (4)	C(65)	9129 (10)	4141 (10)	−100 (14)	6.0 (5)
C(63)	6702 (12)	4378 (9)	−700 (10)	3.4 (4)	C(66)	8888 (11)	4352 (10)	1332 (12)	4.8 (5)
				Perchlorate 1					
O(11)	3710 (12)	−753 (9)	6056 (12)	8.5 (5)	O(13)	2233 (12)	513 (6)	5092 (12)	7.6 (4)
O(12)	1731 (12)	−915 (8)	4710 (15)	9.3 (5)	O(14)	3531 (14)	−680 (10)	3627 (12)	12.4 (6)
				Perchlorate 2					
O(21)	3222 (11)	4460 (6)	−1153 (11)	6.2 (3)	O(23)	1583 (12)	5710 (8)	−1979 (11)	6.8 (4)
O(22)	3633 (13)	5916 (9)	−850 (17)	16.4 (8)	O(24)	2020 (14)	5615 (9)	439 (10)	9.4 (5)
				Norbornadiene 1					
C(1)	1677 (14)	1056 (9)	1495 (10)	5.8 (6)	C(5)	−338 (11)	1477 (11)	59 (16)	5.5 (6)
C(2)	2091 (15)	158 (8)	485 (15)	5.0 (5)	C(6)	109 (14)	1216 (11)	1407 (14)	5.2 (5)
C(3)	1644 (16)	420 (10)	−864 (12)	6.0 (6)	C(7)	1852 (16)	1782 (9)	625 (18)	6.2 (8)
C(4)	973 (15)	1467 (9)	−627 (12)	5.7 (6)					
				Norbornadiene 2					
C(71)	3787 (13)	3525 (8)	4943 (10)	4.5 (5)	C(75)	5055 (11)	3530 (9)	3051 (12)	2.6 (4)
C(72)	3076 (14)	4553 (8)	4806 (11)	3.8 (5)	C(76)	5228 (11)	3461 (9)	4502 (13)	4.2 (5)
C(73)	2904 (13)	4622 (7)	3356 (12)	3.3 (4)	C(77)	3164 (15)	3038 (8)	3653 (16)	6.0 (7)
C(74)	3515 (13)	3634 (8)	2661 (9)	4.1 (5)					

[a] Positional parameters ×10^4.

Rh, As, and N atoms. This conformation may be adopted to minimize steric interactions between the methyl substituents and those on the N atoms. The norbornadiene ligands each occupy two coordination sites on the Rh atoms, and there are no significant differences in their modes of bonding to the metal atom. It may be noted (see Figure 1) that the midpoints of the alkene bonds do not lie in the planes defined by the Rh, As, and N atoms. In molecule 1, the midpoint of C(2)–C(3) is 0.24 Å above the plane, on the same side as C(17), while that of C(5)–C(6) is 0.13 Å below the plane. The analogous values for molecule 2 are the midpoint of C(72)–C(73) 0.26 Å below the plane, and that of C(75)–C(76) is 0.01 Å above the plane, again on the same side as C(47). The norbornadiene ligands are thus twisted in opposite senses with respect to the coordinating plane.

Perspective views of the Rh atoms and the chiral ligands are presented in Figure 2, with the view directions chosen in identical ways. Although the conformations of the chelate rings are very similar, it is clear that the phenyl rings are differently arranged.

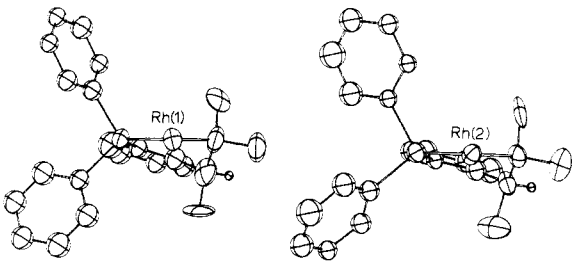


Figure 2. Perspective views of the cations, showing the phenyl ring orientations as viewed from the norbornadiene coordination site.

Results and Discussion

Synthesis and Spectra. The integrity of the chiral C atom of *N,N*-dimethyl-1-phenylethylamine is not affected by reaction with butylithium. The ortho-lithiated amine reacts with either $(C_6H_5)_2AsCl$ or $(C_6H_5)_2PCl$ to give the two chiral, bidentate ligands amars (**1**) and amphos (**2**) (Scheme I). These ligands have been isolated and purified through formation of their HCl salts. The free ligands have been regenerated by treatment with KOH in ethanol.[13] Yields of 30%–60% have been obtained of the air-stable solids, high values compared to the yields obtained for other chiral chelates.[2,4]

The ^{31}P NMR spectra of amphos and amphos·HCl showed only a small difference in chemical shift, consistent with

Table VI. Selected Bond Distances (Å) and Angles (Deg)

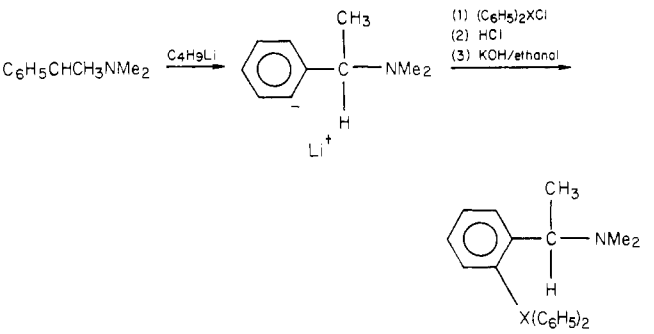
Molecule 1		Molecule 2	
Rh(1)-As(1)	2.393 (3)	Rh(2)-As(2)	2.400 (3)
Rh(1)-N(1)	2.171 (20)	Rh(2)-N(2)	2.182 (16)
Rh(1)-C(2)	2.194 (14)	Rh(2)-C(72)	2.185 (12)
Rh(1)-C(3)	2.204 (14)	Rh(2)-C(73)	2.149 (12)
Rh(1)-C(5)	2.155 (14)	Rh(2)-C(75)	2.084 (13)
Rh(1)-C(6)	2.145 (15)	Rh(2)-C(76)	2.121 (13)
As(1)-C(11)	1.88 (1)	As(2)-C(41)	1.94 (1)
As(1)-C(21)	1.91 (2)	As(2)-C(51)	1.93 (2)
As(1)-C(31)	1.96 (1)	As(2)-C(61)	1.93 (1)
N(1)-C(17)	1.56 (2)	N(2)-C(47)	1.41 (2)
N(1)-C(19)	1.51 (3)	N(2)-C(49)	1.49 (3)
N(1)-C(20)	1.49 (3)	N(2)-C(50)	1.50 (3)
C(17)-C(16)	1.55 (3)	C(47)-C(46)	1.49 (2)
C(17)-C(18)	1.48 (3)	C(47)-C(48)	1.59 (3)
As(1)-Rh(1)-N(1)	89.8 (5)	As(2)-Rh(2)-N(2)	89.6 (5)
C(2)-Rh(1)-C(3)	36.8 (5)	C(72)-Rh(2)-C(73)	37.4 (5)
C(5)-Rh(1)-C(6)	37.7 (5)	C(75)-Rh(2)-C(76)	38.6 (5)
Rh(1)-As(1)-C(11)	113.7 (4)	Rh(2)-As(2)-C(41)	114.9 (4)
Rh(1)-As(1)-C(21)	112.9 (4)	Rh(2)-As(2)-C(51)	119.3 (4)
Rh(1)-As(1)-C(31)	114.9 (4)	Rh(2)-As(2)-C(61)	112.5 (4)
Rh(1)-N(1)-C(17)	112 (1)	Rh(2)-N(2)-C(47)	115 (1)
Rh(1)-N(1)-C(19)	112 (2)	Rh(2)-N(2)-C(49)	111 (1)
Rh(1)-N(1)-C(20)	112 (1)	Rh(2)-N(2)-C(50)	107 (1)
N(1)-C(17)-C(18)	109 (2)	N(2)-C(47)-C(48)	109 (2)
C(16)-C(17)-C(18)	118 (2)	C(46)-C(47)-C(48)	109 (2)
C(16)-C(17)-N(1)	114 (2)	C(46)-C(47)-N(2)	119 (2)

protonation of the N and not the P atom (Table VII). The ^{1}H resonance of the NCH_3 protons of amphos·HCl is concentration dependent. In dilute solution two distinct, sharp doublets are observed for the methyl groups, while in more concentrated samples a single broad peak is seen. A small shift in the ^{31}P resonance also occurs. These effects were attributed to the occurrence of either intramolecular or intermolecular H bonding, between the NH entity and P atom, in dilute and concentrated solutions, respectively. Such bonding would alter the degree of the diastereotopic inequivalence of the methyl groups and thus give rise to the observed signals.

Neutral $[RhCl(ligand)]_2$ and cationic $[Rh(C_7H_8)(ligand)]ClO_4$ complexes were prepared by reacting $[RhCl(C_2H_4)_2]_2$[14] and $[Rh(C_7H_8)_2]ClO_4$,[4] respectively, with the appropriate free ligand. The ^{31}P NMR spectrum of the neutral amphos complex indicates that the cis and trans isomers exist in a 4:1 ratio in solution. The cationic complex of amphos has a single doublet, upfield of the neutral species. This result, and the lower Rh–P coupling constant, are consistent with the positive charge on the metal atom reducing the withdrawal of electron density from the P atom.

Hydrosilation Reactions. The Rh complexes were used as catalysts for the homogeneous hydrosilation of a series of prochiral ketones. In addition, similar cationic species containing the chiral chelates (*S*,*S*)-chiraphos and (+)-diop were used for comparative purposes.

Scheme I



1, X = As; amars
2, X = P; amphos

In a typical procedure, the catalyst was prepared in situ by mixing of $[RhCl(C_2H_4)_2]_2$[14] and the appropriate chiral chelate in benzene. $(C_6H_5)_2SiH_2$ and the ketone were added in that order. The catalyst to substrate ratio was approximately 1:300 or 0.2 mol %. The chiral silyl ether products were isolated by vacuum distillation and their ORD spectra compared to published data.[7] In the case of $C_2H_5CH(CH_3)OSi(C_6H_5)_2H$, an optically pure sample of the *R* isomer was prepared to allow optical yields to be determined. The properties of the isolated silyl ethers are listed in Table VIII.

The results of the ketone reductions are reported in Table IX. In general, the silyl ethers were produced in high chemical yields (>90%). In the reduction of acetophenone, a side product, $CH_2C(C_6H_5)OSi(C_6H_5)_2H$, was detected in varying degree of abundance depending on the catalyst. However, this was the only case where the silyl enol ether was observed.

The reactions catalyzed by complexes of (+)-diop or *R*-amphos gave predominantly the *S* enantiomers of the hydrosilated products. The amphos catalyst gave the best optical yields of the catalysts tested. The highest enantiomeric excess observed was 72%, in the hydrosilation of *tert*-butyl methyl ketone. The chiraphos catalyst gave poor optical yields by comparison. In addition, the configuration of the silyl ether product varied with the substrate for this catalyst. The amars complex catalyzed these reactions but introduced little if any enantiomeric bias into the products.

It is clear from the data that the nature of the chiral chelate ligand has a profound effect on the optical yield. The choice of substrate is also crucial. When the *difference* in steric bulk of the substituents on the ketone is large, we observed high optical yields in that for each catalyst the best optical yields were obtained for reductions of *tert*-butyl methyl ketone and

Table VII. ^{31}P and ^{1}H NMR Data for Ligands and Complexes

	^{1}H NMR data		^{31}P NMR data	
compd	δ	*J*, Hz	δ	*J*, Hz
amphos	6.9-7.6 (m), 4.16 (d of q), 2.04 (s), 1.20 (d)	$\|J_{CH_3-H}\| = 6.0$, $\|J_{CH-P}\| = 6.0$	−20.5	
amars	7.0-7.4 (m), 3.98 (q), 1.92 (s), 1.28 (d)	$\|J_{CH_3-H}\| = 7.0$		
amphos·HCl[a]	6.9-7.6 (m), 5.04 (m), 1.6 (d), 2.70 (br, s) or 2.94 (d), 2.46 (d)	$\|J_{CH_3-H}\| = 8.0$, $\|J_{NCH_3-H}\| = 5.0$	−20.0, −20.8[a]	
amars·HCl	7.0-7.7 (m), 4.74 (q), 2.65 (br, s), 1.64 (d)	$\|J_{CH_3-H}\| = 6.0$		
$[Rh(amphos)Cl]_2$[b]			51.1, 44.2	$\|J_{Rh-P}\| = 183$, $\|J_{Rh-P'}\| = 184$
$[Rh(amphos)(NBD)]ClO_4$			20.8	$\|J_{Rh-P}\| = 172$

[a] The NCH_3 and ^{31}P resonances varied with concentration. [b] The ratio of the two isomers was 80:20, with the more abundant species giving the upfield resonance.

Table VIII. Spectroscopic and Physical Properties of Chiral Silyl Ethers

$RR^1C(H)OSi(C_6H_5)_2H$				^1H NMR[a]		IR[b]
R	R^1	bp, °C (torr)	D, g cm^{-3}	δ	J, Hz	ν(Si-H), cm^{-1}
Ph	Me	140 (0.1)	1.0760	8.0-7.2 (br m), 5.48 (s), 5.10 (q), 1.49 (d)	$\lvert J_{CH_3-CH}\rvert = 7.0$	2130
Ph	Et	145 (0.1)	1.0663	8.0-7.2 (br m), 5.45 (s), 4.84 (t), 1.80 (br m), 0.86 (t)	$\lvert J_{CH_3-CH_2}\rvert = 7.5$, $\lvert J_{CH_2-CH}\rvert = 6.5$	2130
Et	Me	115 (0.1)	0.9994	7.8-7.2 (br m), 4.96 (s), 3.96 (m), 1.50 (m), 1.16 (d), 0.90 (t)	$\lvert J_{CH_3-CH_2}\rvert = 7.5$, $\lvert J_{CH_2-CH}\rvert = 7.0$, $\lvert J_{CH_2-CH}\rvert = 6.0$	2120
t-Bu	Me	110 (0.1)	0.9884	7.8-7.2 (br m), 5.50 (s), 3.63 (q), 1.08 (d), 0.90 (s)	$\lvert J_{CH_3-CH}\rvert = 7.0$	2120
t-Bu	*i*-Pr	122 (0.1)	1.0040	7.8-7.3 (br m), 5.59 (s), 3.38 (d), 3.08 (d), 0.96 (m), 0.94 (s)	$\lvert J_{CH-CH'}\rvert = 3.0$	2125

[a] Recorded in acetone-d_6, except for $C_2H_5CH(CH_3)OSi(C_6H_5)_2H$, where $CDCl_3$ was used. [b] Recorded from neat samples.

Table IX. Asymmetric Hydrosilation of Ketones RR^1CO as Catalyzed by L-L + $[Rh(C_2H_4)_2Cl]_2$

R	R^1	$[\alpha]^{25}_D$[e]	chem yield,[a] %	opt yield,[b] %	config
		L-L = *S*-amphos			
Ph	Me	−14.3	90 (10)[c]	27	*S*
Ph	Et	−11.2	90	18	*S*
Me	Et	6.1	98	27	*S*
t-Bu	Me	6.9	98	72	*S*
t-Bu	*i*-Pr	0	90	0	
		L-L = *R*-amphos			
Ph	Me	17.7	90 (10)	33	*R*
Ph	Et	13.0	90	21	*R*
Me	Et	−6.3	98	27	*R*
t-Bu	Me	−6.3	98	66	*R*
t-Bu	*i*-Pr	0	90	0	
		L-L = (+)-diop			
Ph	Me	−12.5	95 (5)	23	*S*
Ph	Et	−14.5	90	24	*S*
Me	Et	3.2	98	14	*S*
t-Bu	Me	5.9	98	62	*S*
t-Bu	*i*-Pr	0	90	0	
		L-L = *S,S*-chiraphos			
Ph	Me	−2.1	60 (40)	4	*S*
Ph	Et	1.7	90	3	*R*
Me	Et	0	98	0	
t-Bu	Me	1.8	90	19	*S*
t-Bu	*i*-Pr	−2.4	90	*d*	
		L-L = *S*-amars			
Ph	Me	0	75 (25)	0	
Ph	Et	0	85	0	
Me	Et	0	90	0	
t-Bu	Me	−0.76	85	8	*R*
t-Bu	*i*-Pr	2.1	95	*d*	
		Catalyst Precursor [Rh(*S*-amphos)(norbornadiene)]ClO_4			
t-Bu	Me	4.0	95	43	*S*

[a] Based on ^1H NMR of reaction mixture, %. [b] Optical yield; ref 7. [c] The number in brackets refers to % of CH_2=C(Ph)OSiPh$_2$H. [d] Not determined. [e] For silyl ether.

the poorest for *tert*-butyl isopropyl ketone.

In related systems it is generally believed[27,28] that the dissymmetric dispositions of the phenyl rings on the chiral chelate ligand are responsible for the chiral recognition. We therefore assume that the optical induction results when the prochiral substrate molecule binds cis to the P atom in the amphos catalyst. However, in both the amphos and the amars complexes, the two coordination sites are inequivalent. Indeed, the existence of both isomers of the catalyst precursor was demonstrated above, and thus the selectivity of this catalyst will depend upon the relative rates of reaction of the cis and trans isomers. The cationic species [Rh(amphos)(C_7H_8)]ClO_4 gave a lower optical yield than the neutral species. This suggests that the degree of induction may be increased if one could direct coordination of the substrate into the site cis to the P atom. However, conclusive proof for this assertion will only be obtained from kinetic studies.

Perhaps the most startling results we obtained were from the reactions involving the amars catalyst. A minor alteration to the successful amphos catalyst reduced the optical yields to 0. The differences in the degree of discrimination may be affected by electronic factors; however, one would not expect such factors to be responsible for such vast differences in optical yields when the chemical yields are so similar for the two catalysts (Table IX). The X-ray crystallographic study of the Rh–amars complex showed that two independent cations were present in the unit cell, with two different conformations of the ligand observed in the solid state. Each contained phenyl rings in pseudo axial–equatorial arrangements, though in one cation the equatorial ring exposes its face to the cis coordination site while the axial ring displays its edge. The opposite is true in the other cation (Figure 2). On the basis of arguments similar to those of Knowles[27] and Bosnich,[28] it appears that the ability of this aminoarsine chelate ligand to adopt two opposing phenyl ring face–edge conformations (and presumably many other conformations in between) is responsible for the low degrees of optical induction for the catalyst containing this ligand. An alternative explanation might attribute the difference in optical yields between the amphos and amars catalysts to the longer Rh–As and As–C bond lengths. This change in geometry would presumably remove the phenyl rings from close proximity to the cis coordination site and thus reduce their interaction with the substrate molecule.

As yet it is not well understood which of the features of the ligand geometry that change when a P atom replaces the As atom is or are responsible for the asymmetric induction caused by the amphos ligand. Further studies in this area are in progress, and the crystal structure analysis of the [Rh(amphos)(C_7H_8)]ClO_4 catalyst precursor will be reported in due course.[29]

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Registry No. *S*-**1**, 79201-68-6; *S*-**1**·HCl, 79201-69-7; *S*-**2**, 66162-04-7; *S*-**2**·HCl, 79201-70-0; *R*-**2**, 79201-71-1; *R*-**2**·HCl, 79201-72-2; [Rh(*S*-amars)C_7H_8]ClO_4, 79201-48-2; [Rh(*S*-amphos)C_7H_8]ClO_4, 79215-49-9; *cis*-[Rh(*S*-amphos)Cl]$_2$, 79254-36-7; *trans*-[Rh(*S*-amphos)Cl]$_2$, 79297-15-7; (+)-diop, 37002-48-5; *S,S*-chiraphos, 64896-28-2; PhMeCO, 98-86-2; PhEtCO, 93-55-0;

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MeEtCO, 78-93-3; *t*-BuMeCO, 75-97-8; *t*-Bu(*i*-Pr)CO, 5857-36-3; (*R*)-PhMeC(H)OSi$(C_6H_5)_2H$, 55630-27-8; (*S*)-PhMeC(H)OSi$(C_6H_5)_2H$, 79201-73-3; (*R*)-PhEtC(H)OSi$(C_6H_5)_2H$, 55630-28-9; (*S*)-PhEtC(H)OSi$(C_6H_5)_2H$, 79201-74-4; (*R*)-EtMeC(H)OSi$(C_6H_5)_2H$, 79201-75-5; (*S*)-EtMeC(H)OSi$(C_6H_5)_2H$, 79201-76-6; (*R*)-*t*-BuMeC(H)OSi$(C_6H_5)_2H$, 55630-29-0; (*S*)-*t*-BuMeC(H)OSi$(C_6H_5)_2H$, 79201-77-7; (−)-*t*-Bu(*i*-Pr)C(H)OSi$(C_6H_5)_2H$, 79201-78-8; (+)-*t*-Bu(*i*-Pr)C(H)OSi$(C_6H_5)_2H$, 79201-79-9; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; $[Rh(C_7H_8)_2]ClO_4$, 60576-58-1; (*S*)-*N*,*N*-dimethyl-1-phenylethylamine, 17279-31-1; (*R*)-*N*,*N*-dimethyl-1-phenylethylamine, 19342-01-9; $As(C_6H_5)_2Cl$, 712-48-1; $P(C_6H_5)_2Cl$, 1079-66-9; $(C_6H_5)_2SiH_2$, 775-12-2; (*R*)-$C_2H_5CHCH_3OH$, 14898-79-4; *cis*-[Rh(*R*-amphos)Cl]$_2$, 79254-35-6; *trans*-[Rh(*R*-amphos)Cl]$_2$, 79201-50-6.

Supplementary Material Available: Listings of hydrogen atom parameters (Table V) and structure amplitudes (11 pages). Ordering information is given on any current masthead page.

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Transition-Metal Complexes of Poly(1-pyrazolyl)borate Ligands. 3.[1] Triphenylphosphine and Di-*p*-tolyl Disulfide Derivatives of Molybdenum and Tungsten (Hydrotris(1-pyrazolyl)borato)dicarbonyl(arenediazo) Complexes and the Crystal and Molecular Structure of (Hydrotris(1-pyrazolyl)borato)bis(*p*-toluenethiolato)-(*p*-fluorobenzenediazo)molybdenum(II)

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The complexes $HB(pz)_3M(CO)_2N_2Ar$ react with triphenylphosphine in boiling xylene to yield $HB(pz)_3M(CO)(PPh_3)N_2Ar$ (M = Mo, Ar = $C_6H_4CH_3$-*p*, C_6H_4F-*p*; M = W, Ar = $C_6H_4CH_3$-*p*) and with di-*p*-tolyl disulfide under similar conditions to give $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2N_2Ar$ (Ar = $C_6H_4CH_3$-*p*, C_6H_4F-*p*). The crystal and molecular structure of $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4F\text{-}p)$, $C_{29}H_{28}BFMoN_8S_2$, is reported. The crystals are monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14) with four molecules in a unit cell of dimensions a = 8.336 (3) Å, b = 33.655 (8) Å, c = 11.063 (2) Å, and β = 95.16 (1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculation to R_F = 0.056 and R_{wF} = 0.044 for 2816 independent reflections (with $I > 3\sigma(I)$) measured by diffractometer. The molybdenum atom has slightly distorted octahedral coordination with Mo–N(arenediazo) = 1.807 (8) Å, Mo–S = 2.328 and 2.344 (3) Å, Mo–N(pyrazolyl) = 2.193–2.234 (8) Å, N–N = 1.229 (9) Å, Mo–N–N = 170.8 (8)°, and N–N–C = 121.4 (9)°. The dimensions establish that the arenediazo ligand is "singly bent" and are interpreted as indicating a considerable degree of double-bond character in the arenediazo Mo–N bond and intermediate between double- and single-bond character in the Mo-S bonds. The chemical behavior of the bis(*p*-toluenethiolato) complexes is briefly reported.

Introduction

In related pairs of carbonyl complexes containing cyclopentadienide and tris(1-pyrazolyl)borate ligands respectively, it is generally found that derivatives of the latter are more resistant to carbonyl displacement than those of the former. This effect may be due to the greater steric bulk of the $HB(pz)_3^-$ ligand restricting access to the metal center or to stabilization of coordinated CO by the more powerfully electron-donating[3] pyrazolylborate ligand or to a combination of both effects. As shown by King and Bisnette,[4] the arenediazo complex $(\eta\text{-}C_5H_5)Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$ yields the monocarbonyl $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$ when treated with triphenylphosphine in boiling methylcyclohexane (100 °C) and reacts with dimethyl disulfide under similar conditions to give the dinuclear, carbonyl-free $[(\eta\text{-}C_5H_5)Mo(\mu\text{-}SCH_3)N_2C_6H_4CH_3\text{-}p]_2$. In contrast, Trofimenko[5] has reported that the analogous complexes $HB(pz)_3Mo(CO)_2(N_2Ar)$ fail to react with these reagents under similar conditions. We now report that at higher temperatures (xylene, 140 °C) the hydrotris(pyrazolyl)borato complexes will react (albeit very slowly) with triphenylphosphine and di-*p*-tolyl disulfide and describe the complete structural characterization of a novel product of the latter reaction, the *formally* coordinatively unsaturated arenediazo complex $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4F\text{-}p)$.

Experimental Section

The compounds $HB(pz)_3Mo(CO)_2N_2Ar$ (Ar = $C_6H_4CH_3$-*p*, C_6H_4F-*p*) and $HB(pz)_3W(CO)_2(N_2C_6H_4CH_3\text{-}p)$ were prepared by standard literature methods.[5] Other chemicals and solvents were purchased from commercial sources and were used as received. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer and were calibrated with polystyrene film. The 60-MHz ^1H NMR spectra were obtained with a Perkin-Elmer/Hitachi R20-A instrument. Microanalyses were carried out by the staff of the Microanalytical Laboratory of the Chemistry Department, University College.

Reaction of $HB(pz)_3M(CO)_2N_2Ar$ (M = Mo, W) with Triphenylphosphine. A solution of $HB(pz)_3Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$ (1.0 g, 2.07 mmol) and triphenylphosphine (2.72 g, 10.4 mmol) in 40 mL of xylene was refluxed under nitrogen for 3 days. The solvent was removed in vacuo, and the residue was chromatographed on alumina, eluting with CH_2Cl_2. The first red band to elute yielded a trace of unreacted $HB(pz_3Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$ and was followed by a second red band containing the major product of the reaction. Evaporation of the solvent in vacuo and recrystallization of the residue from CH_2Cl_2/hexane gave crystalline $HB(pz)_3Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$ (0.6 g, 40.5% yield): Ir (CH_2Cl_2) $\bar{\nu}$(CO) 1860 (s) cm^{-1}; $\bar{\nu}$(NN) (assignment tentative in the absence of ^{15}N labeling data) 1530, 1485 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 8.23 (d, J = 1 Hz, 1 H) 7.80 (m, 3 H), 7.6–7.3 (m, 15 H), 7.0 (d, J = 2 Hz, 1 H), 6.65 (d, J = 2 Hz, 1 H), 6.30 (t, J = 4 Hz, 1 H), 6.10 (s, 4 H), 5.95 (t, J = 4 Hz, 1 H), 5.80 (t, 4 Hz, 1 H), 2.30 (s, 3 H). Anal. Calcd for $HB(px)_3Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$: C, 58.52; H, 4.46; N, 15.61. Found: C, 58.60; H, 4.47; N, 15.37.

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