

Reactions of Tris(oxazolinyl)phenylborato Rhodium(I) with C-X(X = Cl, Br, OTf) Bonds: Stereoselective Intermolecular Oxidative Addition

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The achiral and enantiopure chiral compounds $To^{M}Rh(CO)_{2}$ (3) and $To^{P}Rh(CO)_{2}$ (4) ($To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate; <math>To^{P} = tris(4S-isopropyl-2-oxazolinyl)phenylborate)$ were prepared to investigate stereoselective oxidative addition reactions and develop new catalytic enantioselective bond functionalization and cross-coupling chemistry. Reactivity at the rhodium center is first shown by the substitution of the carbonyl ligands in 3 and 4 in the presence of the appropriate ligand; thus treatment of $To^{M}Rh(CO)_{2}$ with $P(OMe)_{3}$ provides $To^{M}Rh(CO)[P(OMe)_{3}]$ (5). However, reaction of $To^{M}Rh(CO)_{2}$ and MeOTf ($Tf = SO_{2}CF_{3}$) affords the complex [$\{N-Me-\kappa^{2}-To^{M}\}Rh(CO)_{2}$]OTf (6), resulting from *N*-oxazoline methylation rather than oxidative addition to rhodium(I). In contrast, $To^{M}Rh(CO)_{2}$ reacts with allyl bromide and chloroform, forming the rhodium(III) species ($\kappa^{3}-To^{M}$)Rh($(TO)_{2}$ and CHCl₃ react to give one diastereomer of ($\kappa^{3}-To^{P}$)-Rh(CHCl₂)Cl(CO) (9; 100:3 dr) almost exclusively. To evaluate the reactivity of these rhodium(I) compounds, the carbonyl stretching frequencies have been examined. The data for the mono- and trivalent rhodium oxazolinylborate compounds indicate that the electron-donating ability of [To^{M}]⁻ is slightly greater than that of [To^{P}]⁻, and both ligands provide electronic environments that can be compared to the tris(pyrazolyl)borate ligand family.

Introduction

Oxidative addition of polar C–X bonds is fundamental to organometallic chemistry and is an essential step in homogeneous catalytic processes such as rhodium(I)-catalyzed acetic acid synthesis¹ and iridium(I)-catalyzed allylic substitution.² Proposed mechanistic pathways, including S_N2like nucleophilic substitution, concerted oxidative addition, and radical chain reactions, often depend on conditions, substrates, and ancillary ligands.³ Meanwhile, the intimate mechanism (radical, concerted, or S_N2) can affect the products' stereochemistry, the possibility for stereoselectivity, and application in enantioselective catalytic transformations. CpML₂ and TpML₂ (M = Rh, Ir; Cp = η^5 -C₅R₅, Tp = tris(pyrazolyl)borate) compounds are well known to undergo oxidative addition reactions to give racemic products⁴⁻⁶ or diastereomerically enriched pairs of enantiomers.⁷ Chiral auxiliaries on Cp or Tp have had limited success in affecting stereoselective intermolecular oxidative addition to give enantio-enriched diastereomeric products,⁸⁻¹⁰ although Tp^{menth}Rh(CO)₂ (Tp^{menth} = tris(menthylpyrazolyl)borate) undergoes a stereoselective ligand cyclometalation under photolytic conditions.¹⁰ In another example, a racemic planar-chiral iridium compound oxidatively adds C–H bonds to give a stereogenic iridium center with high diastereoselectivity.¹¹ Also, a resolved planar-chiral iridium(I) complex containing a chiral neomenthyl auxiliary and a linked bulky phosphine forms one diastereomer upon treatment with [Me₃O][BF₄].^{8b}

These reactions provide a foundation for new asymmetric catalysis, and stereoselective oxidative addition reactions will be useful in the development of new reagents and catalysts for

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Scheme 1. Reaction Pathways for the Interaction of To^MRh(CO)₂ (3) with Strong and Weak Electrophiles



enantioselective delivery of alkyl groups to organic substrates. To discover new chemistry along these lines, we prepared the monoanionic tridentate ligands tris(4,4-dimethyl-2-oxazolinyl)phenylborate $[To^M]^-$ and tris(4*S*-isopropyl-2-oxazolinyl)phenylborate $[To^P]^-$. Initially, we synthesized oxazolinylborato iridium(I) compounds with the idea that this ligand platform would allow straightforward structural and electronic variation to optimize selectivity and probe mechanistic aspects of stereochemistry in oxidative addition reactions.¹²

Instead, we observed N-methylation and N-protonation of one oxazoline group upon reaction of these tris(oxazolinyl)borato iridium(I) compounds with the strong electrophiles MeOTf and HOTf. A related N-protonation pathway occurs upon reaction of TpRh(CO)₂ and HBF₄·Et₂ \dot{O} ,¹³ whereas the corresponding iridium compound undergoes a metal-based protonation (formal oxidative addition) to give [TpIrH(CO)₂]-BF₄. In contrast to N-protonation of TpRh(CO)₂, the compounds Tp*Rh(CO)L (Tp* = tris(3,5-dimethylpyrazolyl)borate; L = CO, PMe₃, PMe₂Ph, PMePh₂, PPh₃) and MeI react by oxidative addition to give [Tp*RhI(COMe)L] through an S_N2 pathway.⁵ Interestingly, a related cationic tris(oxazolinyl)ethane rhodium(I) complex $[{tris-ox}Rh(C_8H_{12})]BF_4$ is oxidized by CsBr₃, forming ${tris-ox}RhBr_3$.¹⁴ Although that oxidation reaction does not provide a new stereogenic center, tris-ox ligands provide high enantioselectivity in a range of catalytic processes,¹⁵ including palladium-catalyzed allylic alkylation that involves oxidative addition to {tris-ox}Pd^[0].^{15b} Oxidative addition reactions of chlorocarbons and rhodium(I) compounds containing N,N,N-donor ligands have also been

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described for chelating pybox (pybox = 2,6-bis(4,4-dimethyl-2-oxazolinyl)pyridine) and 2,6-diiminopyridines,^{16,17} as well as three monodentate pyridines.¹⁸ Several of these reactions are proposed to proceed via nucleophilic attack by an electron-rich rhodium(I) center.

An additional complication in rhodium(I) and iridium(I) scorpionate chemistry involves the multiple configurational isomers that can affect reaction pathways, including tridentate coordination and two bidentate boat conformations.¹⁹ Likewise, because our {To^M}M complexes contain metal and oxazoline reactive sites and rapidly equilibrating isomers, it is difficult to predict which product will be formed. Still, because Tp*RhL₂ and MeI react by oxidative addition,⁵ we decided to investigate the reactions of R-X electrophiles and tris(oxazolinyl)borato rhodium dicarbonyl compounds. Here we report the synthesis of achiral $TI[To^{M}]$ (1) and chiral Tl[To^P] (2) as effective ligand transfer agents as well as the corresponding achiral $To^{M}Rh(CO)_{2}$ (3) and enantiopure $To^{P}Rh(CO)_{2}$ (4) compounds. Reactions of these rhodium(I) complexes with electrophiles have been investigated. We found that metal-centered oxidative additions are thermally accessible, N-oxazoline- versus metal-based selectivity is governed by the nature of the electrophile (Scheme 1), and the enantiopure oxazolinylborato rhodium(I) complex reacts with high diastereoselectivity.

Experimental Section

General Procedures. All reactions were performed under an inert atmosphere using standard Schlenk techniques or in a glovebox unless otherwise indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane, diethyl ether, and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under N₂. Benzene-*d*₆ and toluene-*d*₈ were vacuum transferred from Na/K alloy and stored under N₂ in the glovebox. All organic reagents were purchased from Aldrich. Chloroform was distilled from calcium hydride, and allyl bromide was distilled prior to use. $\text{Li[To}^{M}]$, ^{12a} $\text{Li[To}^{P}]$, ^{12b} and [Rh(μ -Cl)(CO)₂]₂²⁰ were prepared by published procedures. ¹H, ¹¹B, and ¹³C{¹H} NMR spectra

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were collected on Bruker DRX-400 and Avance II-700 spectrometers. ¹H and ¹³C{¹H} resonances were assigned using standard 2D methods, including COSY, ¹H-¹³C HMQC, and ¹H-¹³C HMBC experiments. ¹⁵N chemical shifts were determined by ¹H-¹⁵N HMBC experiments on a Bruker Avance II-700 spectrometer with a Bruker Z-gradient inverse TXI ¹H/¹³C/¹⁵N 5 mm cryoprobe. ¹⁵N chemical shifts were originally referenced to liquid NH₃ and recalculated to the CH₃NO₂ chemical shift scale by adding -381.9 ppm. ¹¹B NMR spectra were referenced to an external sample of BF₃·Et₂O. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility. X-ray diffraction data were collected on a Bruker APEX2 CCD diffractometer.

 $TI[To^{M}]$ (1). Thallium nitrate (4.50 g, 16.9 mmol) was placed in a 500 mL round-bottom flask and dissolved in a water/ methylene chloride mixture (1:1, 200 mL). In a separate flask, $Li[To^{M}]$ (5.87 g, 15.1 mmol) was dissolved in a minimal amount of THF (70 mL). The Li[To^M] solution was added to the Tl[NO₃] solution to produce a white precipitate. This mixture was vigorously stirred for 30 min, and then the precipitate was allowed to settle and the liquid separated into aqueous and organic layers. The aqueous layer was decanted, and the organic layer was washed with water $(3 \times 100 \text{ mL})$ to remove the precipitate. The volatiles from the organic layer were evaporated under reduced pressure to give a viscous yellow oil. This oil was triturated with pentane (5 \times 40 mL), precipitating a pure white product (5.47 g, 9.33 mmol, 61.7%), which was used for further syntheses. Recrystallization from toluene at -35 °C gave analytically pure, white crystalline blocks suitable for X-ray diffraction (4.87 g, 8.32 mmol, 55.0%). ¹H NMR (benzene-d₆, 400 MHz): $\delta 8.36 (d, 2 H, {}^{3}J_{HH} = 7.6 Hz, ortho-C_{6}H_{5}), 7.58 (t, 2 H, C_{6}H_{5})$ ${}^{3}J_{\rm HH} = 7.6$ Hz, meta-C₆H₅), 7.37 (t, 1 H, ${}^{3}J_{\rm HH} = 7.6$ Hz, para-C₆H₅), 3.41 (s, 6 H, CNCMe₂CH₂O), 1.03 (s, 18 H, CNC-Me₂CH₂O). ¹³C{¹H} NMR (benzene- d_6 , 100 MHz): δ 190.5 (br, CNCMe₂CH₂O), 146.7 (br, *ipso*-C₆H₅), 136.59 (ortho-C₆H₅), 126.98 (meta-C₆H₅), 125.56 (para-C₆H₅), 79.83 (CNCMe₂-CH₂O), 66.71 (CNCMe₂CH₂O), 28.84 (CNCMe₂CH₂O). ¹¹B NMR (benzene- d_6 , 128 MHz): δ -16.0 (br s). ¹⁵N{¹H} NMR (benzene- d_6 , 71 MHz): δ -117.3 (${}^{1}J_{\text{TIN}}$ = 795 Hz). IR (KBr, cm⁻¹): ν 3071 (m), 3039 (m), 2963 (s), 2928 (s), 2889 (s), 1600 $(s, \nu_{CN}), 1460 (s), 1430 (m), 1381 (m), 1363 (s), 1348 (m), 1258 (s),$ 1187 (s), 1133 (s), 1014 (w), 967 (s), 926 (w), 890 (w), 809 (w), 744 (w), 706 (s). Anal. Calcd for C₂₁H₂₉BN₃O₃Tl: C, 42.99; H, 4.98; N, 7.16. Found: C, 43.04; H, 4.63; N, 6.74. Mp: 218-220 °C.

Tl[To^P] (2). A suspension of Li[To^P] (1.38 g, 3.20 mmol) and Tl[OAc] (1.26 g, 4.78 mmol) was stirred in CH₂Cl₂ (100 mL) at room temperature overnight. The reaction mixture was then filtered to remove excess Tl[OAc] and Li[OAc], and the filtrate was evaporated under reduced pressure. The residue was crystallized from a concentrated diethyl ether solution at -80 °C to afford $\mathbf{2}$ as a white powder (1.26 g, 2.00 mmol, 62.6%). ¹H NMR (benzene- d_6 , 400 MHz): δ 8.28 (d, 2 H, ${}^{3}J_{\text{HH}} = 7.2$ Hz, ortho- C_6H_5), 7.57 (t, 2 H, ${}^{3}J_{HH} = 7.6$ Hz, meta- C_6H_5), 7.35 (t, 1 H, ${}^{3}J_{HH} = 7.2$ Hz, para- C_6H_5), 3.69 (m, 3 H, CNC(CHMe₂)-HCH₂O), 3.51 (m, 6 H, CNC(CHMe₂)HCH₂O), 1.49 (m, 3 H, CNC(C*H*Me₂)HCH₂O), 0.76 (d, 9 H, ${}^{3}J_{HH} = 6.8$ Hz, CNC-(CH*M*e₂)HCH₂O), 0.67 (d, 9 H, ${}^{3}J_{HH} = 6.8$ Hz, CNC-(CH*M*e₂)HCH₂O). ${}^{13}C{}^{1}H$ NMR (benzene-*d*₆, 150 MHz): δ 136.46 (ortho-C₆H₅), 127.03 (meta-C₆H₅), 125.52 (para-C₆H₅), 71.51 (CNC(CHMe₂)HCH₂O), 70.07 (CNC(CHMe₂)HCH₂O), 33.25 (CNC(CHMe₂)HCH₂O), 19.42 (CNC(CHMe₂)HCH₂O), 18.65 (CNC(CH*Me*₂)HCH₂O). ¹¹B NMR (benzene- d_6 , 128 MHz): δ -19.2. IR (KBr, cm⁻¹): ν 3046 (m), 2955 (s), 1590 (s, $\nu_{\rm CN}$), 1465 (m), 1430 (w), 1387 (w), 1367 (w), 1263 (w), 1166 (m), 1111 (m), 1036 (w), 969 (m), 735 (w), 730 (w), 702 (m). Anal. Calcd for C₂₄H₃₅BN₃O₃Tl: C, 45.85; H, 5.61; N, 6.68. Found: C, 46.08; H, 5.53; N, 6.61. Mp: 70-73 °C, dec.

 $To^{M}Rh(CO)_{2}$ (3). Benzene (50 mL) was added to a solid mixture of Tl[To^M] (0.63 g, 1.07 mmol) and [Rh(μ -Cl)(CO)₂]₂ (0.21 g, 0.54 mmol). The resulting mixture was allowed to stir at

room temperature for 24 h and then filtered. The solvent was evaporated under vacuum. The residue was dissolved in diethyl ether, stirred for 2 h, and then filtered. The filtrate was evaporated to dryness to give To^MRh(CO)₂ as a pale green solid in excellent yield (0.53 g, 0.98 mmol, 92%). X-ray quality crystals were obtained from slow evaporation of a diethyl ether solution. ¹H NMR (benzene- d_6 , 400 MHz): δ 8.08 (d, 2 H, ³ $J_{HH} = 7.2$ Hz, ortho-C₆H₅), 7.51 (t, 2 H, ${}^{3}J_{HH} = 7.6$ Hz, meta-C₆H₅), 7.34 (t, 1 H, ${}^{3}J_{HH} = 7.2$ Hz, para-C₆H₅), 3.50 (s, 6 H, CNCMe₂CH₂O), 1.07 (s, 18 H, CNCMe₂CH₂O). ${}^{13}C{}^{1}H{}$ NMR (benzene-d₆, 150 MHz): δ 188.42 (d, CO, ${}^{1}J_{RhC} = 66.6$ Hz), 135.80 (ortho-C₆H₅), 127.40 (meta-C₆H₅), 126.12 (para-C₆H₅), 79.78 (CNCMe₂-CH₂O), 67.60 (CNCMe₂CH₂O), 28.70 (CNCMe₂CH₂O). ¹¹B NMR (benzene- d_6 , 128 MHz): $\delta -17.3$. ¹⁵N{¹H} NMR (benzene- d_6 , 71 MHz): $\delta -163.1$. IR (KBr, cm⁻¹): ν 2966 (s), 2933 (m), 2070 (s, v_{CO}), 2048 (m, v_{CO}), 2010 (s, v_{CO}), 1997 (s, $\nu_{\rm CO}$), 1968 (m, $\nu_{\rm CO}$), 1616 (m, $\nu_{\rm CN}$), 1571 (s, $\nu_{\rm CN}$), 1361 (m), 1288 (m), 1204 (m), 965 (m). IR (CH_2Cl_2 , cm^{-1}): ν 2963 (m), 2927 (w), 2069 (s, ν_{CO}), 2055 (w sh, ν_{CO}) 2010 (w), 1994 (s, ν_{CO}), 1967 (w), $1616 (w), 1566 (m, \nu_{CN}), 1461 (w), 1360 (w), 1289 (w), 1202 (m),$ 963 (m), 736 (m), 706 (m). Anal. Calcd for C₂₃H₂₉BRhN₃O₅: C, 51.04; H, 5.40; N, 7.76. Found: C, 51.51; H, 5.41; N, 7.76. Mp: 204-206 °C, dec.

 $To^{P}Rh(CO)_{2}$ (4). A 20 mL vial was charged with 2 (0.21 g, 0.34 mmol), $[Rh(\mu-Cl)(CO)_2]_2$ (0.07 g, 0.17 mmol), and benzene (10 mL). The reaction mixture was allowed to stir at room temperature for 6 h and was then filtered. All volatiles were removed to afford 4 as a dark green solid (0.19 g, 0.33 mmol, 95%). ¹H NMR (benzene- d_6 , 400 MHz): δ 8.15 (d, 2 H, ³ $J_{\rm HH}$ = 7.2 Hz, *ortho*-C₆H₅), 7.44 (t, 2 H, ${}^{3}J_{HH} = 7.4$ Hz, *meta*-C₆H₅), 7.25 (t, 1 H, ${}^{3}J_{HH} = 7.4$ Hz, *para*-C₆H₅), 3.64 (m, 9 H, overlapping CNC(CHMe₂)HCH₂O), 2.02 (m, 3 H, CNC(CHMe₂)HCH₂O), 0.72 (d, 9 H, ${}^{3}J_{\text{HH}} = 6.8$ Hz, CNC(CHMe₂)HCH₂O), 0.66 $(d, 9 \text{ H}, {}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, \text{CNC}(\text{CH}Me_2)\text{HCH}_2\text{O}).$ ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (benzene- d_6 , 150 MHz): δ 186.11 (d, CO, ${}^1J_{RhC} = 65.0$ Hz), 134.86 (ortho-C₆H₅), 127.68 (meta-C₆H₅), 126.28 (para-C₆H₅), 74.51 (CNC(CHMe₂)HCH₂O), 67.69 (CNC(CHMe₂)HCH₂O), 32.00 (CNC(CHMe₂)HCH₂O), 19.28 (CNC(CHMe₂)HCH₂O), 15.85 $(CNC(CHMe_2)HCH_2O)$. ¹¹B NMR (benzene- d_6 , 128 MHz): $\delta = 17.3$. ¹⁵N{^TH} NMR (benzene- d_6 , 71 MHz): $\delta = 182.8$. IR (KBr, cm⁻¹): ν 2959 (m), 2898 (w), 2873 (w), 2072 (s, ν_{CO}), 2002 (s, $\nu_{\rm CO}$), 1572 (m, $\nu_{\rm CN}$), 1480 (w), 1464 (w), 1366 (w), 1210 (m), 1180 (w), 1134 (w), 1118 (w), 983 (m), 961 (m), 737 (w). IR (CH₂Cl₂, cm⁻¹): ν 2961 (w), 2077 (s, ν_{CO}), 2007 (s, ν_{CO}), 1575 (m, ν_{CN}), 1481 (w), 1366 (w), 1277 (w), 1209 (w), 1118 (w). Anal. Calcd. for C₂₆H₃₅BRhN₃O₅: C, 53.54; H, 6.05; N, 7.20. Found: C, 53.91; H, 5.54; N, 6.99. Mp: 80-82 °C, dec.

 $To^{M}Rh(CO)[P(OMe)_{3}]$ (5). $P(OMe)_{3}$ (22 μ L, 0.19 mmol) and To^MRh(CO)₂ (100 mg, 0.185 mmol) were dissolved in benzene (10 mL) and allowed to stir for 10 min. All volatiles were removed under vacuum to give To^MRh(CO)[P(OMe)₃] as a pale yellow solid in quantitative yield. X-ray quality crystals were obtained by slow diffusion of pentane into a concentrated toluene solution at -80 °C. ¹H NMR (dichloromethane- d_2 , 400 MHz): δ 7.27 (d, 2 H, ³ J_{HH} = 6.8 Hz, ortho-C₆H₅), 7.13 (t, 2 H, ${}^{3}J_{HH} = 6.8$ Hz, meta-C₆H₅), 7.03 (t, 1 H, ${}^{3}J_{HH} = 6.4$ Hz, *para*-C₆H₅), 3.88 (s, 6 H, CNCMe₂CH₂O), 3.54 (d, 9 H, ${}^{3}J_{PH} = 12.4$ Hz, P(OMe)₃), 1.27 (s, 18 H, CNC- Me_2CH_2O). ¹³C{¹H} NMR (benzene- d_6 , 175 MHz): δ 189.63 (dd, CO, ${}^{1}J_{RhC} = 69.8 \text{ Hz}$, ${}^{2}J_{PC} = 27.5 \text{ Hz}$, 135.68 (*ortho*-C₆H₅), 127.20 (meta-C₆H₅), 125.46 (para-C₆H₅), 78.98 (CNCMe₂CH₂O), 68.16 $(CNCMe_2CH_2O)$, 51.82 (P(OMe)₃), 28.84 (CNC Me_2CH_2O). ¹¹B NMR (benzene- d_6 , 128 MHz): $\delta - 16.4$. ³¹P{¹H} NMR (benzene d_6 , 162 MHz): $\delta -90.0$ (d, ${}^1J_{RhP} = 247.7$ Hz). IR (KBr, cm⁻¹): ν 2966 (s), 1995 (s, $\nu_{\rm CO}$), 1965 (m, $\nu_{\rm CO}$), 1610 (m, $\nu_{\rm CN}$), 1576 (s, $\nu_{\rm CN}$), 1462 (m), 1368 (m), 1279 (m), 1120 (s), 1017(s), 970 (m). Anal. Calcd for C₂₅H₃₈BRhN₃O₇P: C, 47.12; H, 6.01; N, 6.59. Found: C, 47.17; H, 5.93; N, 6.52. Mp: 159–163 °C, dec.

[{N-Me- κ^2 -To^M}Rh(CO)₂]OTf (6). A benzene solution of To^MRh(CO)₂(0.052 g, 0.096 mmol) and MeOTf (0.063 g, 0.35 mmol) was stirred for 30 min and then evaporated to dryness. The residue

was crystallized from a benzene/pentane solution at room temperature to give green, X-ray quality crystals (0.038 g, 0.053 mmol, 55%). Trituration of the crystals with pentane provides a white powder without loss in yield. ¹H NMR (dichloromethane- d_2 , 400 MHz): δ 7.30 (m, 3 H, *para*- and *meta*-C₆H₅), 7.14 (d, 2 H, ${}^{3}J_{HH} = 6.4$ Hz, ortho-C₆H₅), 4.48 (s, 2 H, CN(Me)CMe₂CH₂O), 4.29 (d, 2 H, ${}^{3}J_{HH} = 9.0$ Hz, CN(Rh)CMe₂CH₂O), 4.25 (d, 2 H, ${}^{3}J_{HH} = 9.0$ Hz, CN(Ph/CM)CMe₂CH₂O), 4.25 (d, 2 H, ${}^{3}J_{HH} = 9.0$ Hz, CN(Rh)CMe₂CH₂O), 2.90 (s, 3 H, NCH₃), 1.51 (s, 6 H, CN-(Me)C Me_2 CH₂O), 1.44 (s, 6 H, CN(Rh)C Me_2 CH₂O), 1.41 (s, 6 H, CN(Rh)C Me_2 CH₂O). ¹³C{¹H} NMR (dichloromethane- d_2 , 175 MHz): δ 183.85 (d, CO, ${}^{1}J_{RhC} = 68.3$ Hz), 133.35 (ortho-C₆H₅), 128.77 (meta-C₆H₅), 127.76 (para-C₆H₅), 121.54 (q, ${}^{1}J_{FC} = 319$ Hz, OSO₂CF₃), 82.19 (CN(Me)CMe₂CH₂O), 81.25 (CN(Rh)CMe₂-CH₂O), 69.21 (CN(Rh)CMe₂CH₂O), 67.30 (CN(Me)CMe₂-CH₂O), 30.16 (NCH₃), 28.65 (CN(Rh)CMe₂CH₂O), 28.25 (CN(Rh)C Me_2 CH₂O), 24.45 (CN(Me)C Me_2 CH₂O). ¹¹B NMR (dichloromethane- d_2 , 128 MHz): $\delta -17.3$. ¹⁵N{¹H} NMR (dichloromethane- d_2 , 71 MHz): δ -179.7 (NRh), -211.0 (NMe). IR (KBr, cm⁻¹): ν 3074 (m), 2971 (s), 2083 (s, ν_{CO}), 2012 (s, ν_{CO}), $1580 (s, v_{CN}), 1551 (m, v_{CN}), 1462 (s), 1434 (m), 1390 (m), 1372 (m),$ 1362 (m), 1325 (m), 1262 (s), 1224 (s), 1205 (s), 1157 (s), 1031 (s), 998 (m), 964 (s), 748 (m), 736 (m), 710 (m). Anal. Calcd for C24H32N3O8SF3RhB: C, 41.58; H, 4.65; N, 6.06. Found: C, 42.00;

H, 4.56; N, 5.70. Mp: 132–134 °C, dec. (κ^3 -To^M)Rh(η^1 -C₃H₅)Br(CO) (7). Excess allyl bromide (1.9 mL) and To^MRh(CO)₂ (0.114 g, 0.211 mmol) were allowed to react in benzene for 5 h at room temperature. The solution was filtered, the volatiles were evaporated, and the solid residue was crystallized from a concentrated acetonitrile solution at -30 °C overnight to give a yellow solid (0.063 g, 0.098 mmol, 47%). ¹H NMR (benzene- d_6 , 400 MHz, cis and trans designations for oxazoline rings are given with respect to η^1 -C₃H₅ moiety): δ 8.25 (d, 2 H, $^3J_{HH} = 7.2$ Hz, *ortho*-C₆H₅), 7.53 (t, 2 H, ${}^{3}J_{HH} = 7.2$ Hz, *meta*-C₆H₅), 7.35 (t, 1 H, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, para-C_{6}\text{H}_{5}), 6.99 \text{ (m, 1 H, RhCH}_{2}CHCH_{2}), 5.58 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.8 \text{ Hz}, \text{RhCH}_{2}CHCH_{2}), 5.24 \text{ (d, 1 H, }{}^{3}J_{\text{HH}} = 16.$ 9.6 Hz, RhCH₂CHCH₂), 4.57 (br, 1 H, RhCH₂CHCH₂), 3.66 (d, $1 \text{ H}, {}^{2}J_{\text{HH}} = 8.4 \text{ Hz}, cis-CNCMe_{2}CH_{2}O), 3.64 (br, 1 \text{ H}, RhCH_{2}-$ CHCH₂), 3.40 (d, 1 H, ${}^{2}J_{HH} = 8.0$ Hz, *cis*-CNCMe₂CH₂O), 3.35 $(d, 1 H, {}^{2}J_{HH} = 8.4 Hz, cis-CNCMe_{2}CH_{2}O), 3.24 (d, 1 H, {}^{2}J_{HH} =$ 8.0 Hz, cis-CNCMe₂CH₂O), 3.21 (s, 2 H, trans-CNCMe₂CH₂O), 1.50 (s, 3 H, cis-CNCMe₂CH₂O), 1.44 (s, 3 H, cis-CNCMe₂CH₂O), 1.33 (s, 3 H, cis-CNCMe2CH2O), 1.31 (s, 3 H, cis-CNCMe2CH2O), 1.04 (s, 3 H, trans-CNCMe2CH2O), 0.81 (s, 3 H, trans-CNC-Me₂CH₂O). ¹³C{¹H} NMR (benzene-d₆, 175 MHz, cis and trans designations for oxazoline groups are given with respect to η^1 -C₃H₅ moiety): δ 186.45 (d, CO, ${}^{1}J_{RhC}$ = 59.5 Hz), 148.03 (RhCH₂-CHCH₂), 136.34 (ortho-C₆H₅), 127.32 (meta-C₆H₅), 126.44 (para-C₆H₅), 112.97 (RhCH₂CHCH₂), 81.94 (cis-CNCMe₂CH₂O), 81.22 (cis-CNCMe₂CH₂O), 80.62 (trans-CNCMe₂CH₂O), 73.06 (cis-CN-CMe₂CH₂O), 70.65 (cis-CNCMe₂CH₂O), 69.30 (trans-CNCMe₂-CH₂O), 29.06 (cis-CNCMe₂CH₂O), 28.88 (cis-CNCMe₂CH₂O), 27.19 (cis-CNCMe2CH2O), 27.10 (trans-CNCMe2CH2O), 26.62 (*trans*-CNC Me_2 CH₂O), 25.92 (*cis*-CNC Me_2 CH₂O), 20.53 (d, Rh-CH₂CHCH₂, $J_{RhC} = 15.8$ Hz). ¹¹B NMR (benzene- d_6 , 128 MHz): δ -18.0. ¹⁵N{¹H} NMR (benzene- d_6 , 71 MHz): $\delta - 163.5$ (*cis*), -187.8 (*cis*), -203.5 (*trans*). IR (KBr, cm⁻¹): ν 2967 (m), 2930 (m), 2058 $(s, v_{CO}), 1582 (s, v_{CN}), 1462 (m), 1387 (w), 1367 (m), 1290 (m), 1203$ (m), 968 (m). Anal. Calcd for C25H34N3O4RhBBr: C, 47.35; H, 5.40; N, 6.63. Found: C, 47.09; H, 5.39; N, 6.58. Mp: 174-178 °C, dec.

 $(\kappa^3-\text{To}^{M})$ Rh(CHCl₂)Cl(CO) (8). A solution of To^MRh(CO)₂ (0.107 g, 0.20 mmol) in CHCl₃ (30 mL) was degassed by three freeze-pump-thaw cycles and then heated at 60 °C for 18 h. The reaction mixture was allow to cool to ambient temperature, and then it was filtered. The solvent was removed from the filtrate under reduced pressure, and the residue was extracted with toluene (10 mL) and evaporated to dryness. The resulting solid was washed with CH₃CN (ca. 1 mL) at -30 °C to give an off-white solid (0.054 g, 0.080 mmol, 43%). ¹H NMR (benzene-*d*₆, 400 MHz, *cis* and *trans* designations for oxazoline rings are given with respect to CHCl₂ moiety): δ 8.18 (d, 2 H, ³*J*_{HH} = 7.2 Hz, *ortho*-C₆H₅), 7.81 $(d, 1 H, {}^{2}J_{RhH} = 3.2 Hz, CHCl_{2}), 7.50 (t, 2 H, {}^{3}J_{HH} = 7.6 Hz, meta C_6H_5$), 7.34 (t, 1 H, ${}^{3}J_{HH} = 7.2$ Hz, para- C_6H_5), 3.60 (d, 1 H, ${}^{2}J_{HH} = 8.4$ Hz, cis-CNCMe₂CH₂O), 3.33 (m, 5 H, CNCMe₂-CH2O), 1.60, (s, 3 H, trans-CNCMe2CH2O), 1.51 (s, 3 H, cis-CNCMe2CH2O), 1.29 (s, 3 H, cis-CNCMe2CH2O), 1.28 (s, 3 H, cis-CNC Me_2 CH₂O), 1.11 (s, 3 H, *cis*-CNC Me_2 CH₂O), 0.63 (s, 3 H, *trans*-CNC Me_2 CH₂O). ¹³C{¹H} NMR (benzene- d_6 , 175 MHz): δ 188.42 (d, CO, ${}^{1}J_{RhC} = 59.5$ Hz), 135.19 (*ortho*-C₆H₅), 127.38 (meta-C₆H₅), 126.70 (para-C₆H₅), 82.04 (cis-CNCMe₂CH₂O), 80.77 (cis-CNCMe₂CH₂O), 79.76 (trans-CNCMe₂CH₂O), 73.08 (*cis*-CNCMe₂CH₂O), 71.41 (*cis*-CNCMe₂CH₂O), 68.88 (*trans*-CNCMe₂CH₂O), 63.74 (d, CHCl₂, ${}^{1}J_{RhC} = 26.3$ Hz), 28.87 (*cis*-CNCMe₂CH₂O), 28.71 (*cis*-CNCMe₂CH₂O), 27.48 (*trans*-CNC- Me_2 CH₂O), 26.96 (*cis*-CNC Me_2 CH₂O), 23.68 (*trans*-CNC Me_2 -CH₂O), 21.08 (*cis*-CNC Me_2 CH₂O). ¹¹B NMR (benzene- d_6 , 128 MHz): $\delta - 17.8$. ¹⁵N{¹H} NMR (benzene- d_6 , 71 MHz): $\delta - 177.6$ (cis), -187.8 (cis), -198.0 (trans). IR (KBr, cm⁻¹): ν 3076 (m), 3042 (m), 2985 (s), 2969 (s), 2890 (s), 2088 (s, $\nu_{\rm CO}$), 2042 (w), 2037 (w), 1575 (s, $\nu_{\rm CN}$), 1548 (m), 1496 (m), 1464 (s), 1433 (m), 1388 (s), 1358 (s), 1293 (s), 1273 (s), 1251 (s), 1199 (s), 1155 (s), 1114 (s), 1036 (m), 1024 (m), 957 (s), 933 (s), 891 (m), 800 (m), 785 (m). Anal. Calcd for C₂₃H₃₀BN₃O₄Cl₃BRh: C, 43.67; H, 4.78; N, 6.64. Found: C, 43.20; H, 4.52; N, 6.46. Mp: 156-159 °C, dec.

 $(\kappa^3 - To^P)Rh(CHCl_2)Cl(CO)$ (9). A solution $To^PRh(CO)_2$ (0.102 g, 0.175 mmol) in CHCl₃ (20 mL) was degassed by three freeze-pump-thaw cycles and then allowed to stir overnight at room temperature. All volatiles were evaporated and the residue was purified by silica gel column chromatography, eluting with hexane/ethyl acetate (85:15) to yield a yellow solid (0.060 g, 0.089 mmol, 51%). ¹H NMR (CDCl₃, 400 MHz, cis and trans designations for oxazoline rings are given with respect to CHCl₂ moiety): δ 7.65 (d, 2 H, ${}^{3}J_{HH} =$ 7.6 Hz, ortho-C₆H₅), 7.31 (t, 2 H, ${}^{3}J_{HH} =$ 7.2 Hz, meta-C₆H₅), 7.25 (t, 1 H, ${}^{3}J_{HH} =$ 7.2 Hz, para-C₆H₅), 7.11 (d, 1 H, ${}^{2}J_{RhH} =$ 3.2 Hz, CHCl₂), 4.95 (m, 1 H, cis-CNC(CHMe₂)HCH₂O), 4.84 (m, 1 H, cis-CNC(CHMe₂)H-CH₂O), 4.38 (m, 4 H, overlapping cis- and trans-CNC(CHMe₂)-HCH₂O), 4.28 (t, 1 H, ${}^{2}J_{HH} = 9.6$ Hz, trans-CNC(CHMe₂)-HCH₂O), 4.09 (t, 1 H, ${}^{2}J_{HH} = 9.6$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 4.07 (m, 1 H, trans-CNC(CHMe2)HCH2O), 2.84 (m, 1 H, trans-CNC(CHMe₂)HCH₂O), 2.37 (m, 1 H, *ital*: CNC(CHMe₂)HCH₂O), 2.37 (m, 1 H, *its*-CNC(CHMe₂)HCH₂O), 2.17 (m, 1 H, *cis*-CNC(CHMe₂)HCH₂O), 1.02 (d, 3 H, ${}^{3}J_{HH} = 6.8$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.92 (d, 3 H, ${}^{3}J_{HH} = 6.8$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.86 (d, 3 H, ${}^{3}J_{HH} = 7.2$ Hz, *trans*-CNC(CHMe₂)HCH₂O), 0.75 (d, 3 H, ${}^{3}J_{HH} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 3 H, ${}^{3}J_{HH} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 3 H, ${}^{3}J_{HH} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.75 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, *cis*-CNC(CHMe₂)HCH₂O), 0.65 (d, 2 H, ${}^{3}J_{H} = 6.4$ Hz, $(CHMe_2)HCH_2O)$, 0.65 (d, 3 H, ${}^{3}J_{HH} = 6.8$ Hz, *cis*-CNC(CHMe_2)-HCH_2O), 0.56 (d, 3 H, ${}^{3}J_{HH} = 6.8$ Hz, *trans*-CNC(CHMe_2)-HCH₂O). ¹³C{¹H} NMR (CDCl₃, 175 MHz): δ 179.71 (d, CO, ${}^{1}J_{\text{RhC}} = 59.5 \,\text{Hz}$, 134.84 (ortho-C₆H₅), 127.22 (meta-C₆H₅), 126.63 (para-C₆H₅), 71.73 (trans-CNC(CHMe₂)HCH₂O), 70.71 (cis-CNC(CHMe₂)HCH₂O), 70.25 (trans-CNC(CHMe₂)HCH₂O), 69.69 (cis-CNC(CHMe₂)HCH₂O), 68.42 (cis-CNC(CHMe₂)-HCH₂O), 65.67 (d, CHCl₂, ${}^{1}J_{RhC} = 28.0$ Hz), 65.14 (*cis*-CNC-(CHMe₂)HCH₂O), 29.17 (cis-CNC(CHMe₂)HCH₂O), 29.01 (cis-CNC(CHMe₂)HCH₂O), 28.64 (trans-CNC(CHMe₂)HCH₂O), 20.03 (cis-CNC(CHMe2)HCH2O), 19.17 (cis-CNC(CHMe2)-HCH2O), 18.81 (trans-CNC(CHMe2)HCH2O), 14.71 (cis-CNC-(CHMe₂)HCH₂O), 14.00 (cis-CNC(CHMe₂)HCH₂O), 13.82 (trans-CNC(CHMe2)HCH2O). ¹¹B NMR (CDCl₃, 128 MHz): δ -18.1. ¹⁵N{¹H} NMR (CDCl₃, 71 MHz): δ -194.2 (trans-CNC(CHMe₂)HCH₂O), -204.3 (cis-CNC(CHMe₂)HCH₂O), -217.7 (*cis*-CNC(CHMe₂)HCH₂O). IR (KBr, cm⁻¹): ν 3001 (w), 2962 (m), 2929 (m), 2872 (m), 2092 (s, $\nu_{\rm CO}$), 1590 (s, $\nu_{\rm CN}$), 1479 (w), 1463 (w), 1372 (w), 1364 (w), 1223 (m). Anal. Calcd for C₂₆H₃₆BN₃O₄RhCl₃: C, 46.29; H, 5.38; N, 6.23; Found: C, 46.11; H, 5.03; N, 5.99. Mp: 116-118 °C, dec.

Results and Discussion

Synthesis and Characterization of Tl[To^M] (1), Tl[To^P] (2), To^MRh(CO)₂(3), and To^PRh(CO)₂(4). Following an adaptation



Figure 1. ORTEP diagram of $Tl[To^{M}]$ (1). H atoms are not shown. Relevant bond distances (Å): Tl1-N1, 2.550(4); Tl1-N2, 2.543(5); Tl1-N3, 2.498(5).

of Venanzi's preparation of tris(pyrazolyl)borato rhodium(I) dicarbonyl,^{19a,c} reaction of Li[To^M] and [Rh(μ -Cl)(CO)₂]₂ in acetonitrile at -40 °C yields To^MRh(CO)₂ (**3**), but several impurities also are formed. We previously found that reaction of 2 equiv of Li[To^M] and [Ir(μ -Cl)(C₈H₁₂)]₂ in benzene or THF provides a dimeric LiCl adduct, (LiCl)₂[(κ ²-To^MIr-(η ⁴-C₈H₁₂)]₂.^{12c} We suspected that LiCl was interfering in the synthesis of the corresponding rhodium(I) compounds. Therefore, **1** was prepared as an alternative [To^M]-transfer agent by reaction of Li[To^M] and Tl[NO₃] (eq 1).



The ¹H NMR spectrum of 1 in benzene- d_6 contained singlet resonances for methyl and methylene groups. This spectrum is consistent with a freely rotating phenyl group and a pseudo $C_{3\nu}$ symmetric structure. Cross-peaks were detected between the oxazoline nitrogen and the ring methyl and methylene groups in a ¹H-¹⁵N HMBC experiment (performed with ¹⁵N natural abundance) that provided the ¹⁵N NMR chemical shift (-117 ppm) and ${}^{1}J_{\text{TIN}} = 795$ Hz. These data are consistent with N,N,Ncoordination to thallium. For comparison, the ¹⁵N NMR chemical shift of 2*H*-4,4-dimethyl-2-oxazoline is -127.9.^{12c} The downfield ¹⁵N NMR chemical shift for 1 contrasts the upfield chemical shifts of all of the transition-metal compounds containing the $[To^{M}]^{-}$ ligand that we have prepared, measured, and reported.^{12,21} Only one v_{CN} band (1600 cm⁻¹) for the three oxazoline groups was observed in the infrared spectrum of 1. These IR data also provide support for the coordination of all three oxazolines to thallium. An X-ray crystal structure confirmed the tridentate coordination mode in the solid state (Figure 1).

In addition to verifying the connectivity of **1**, the X-ray structure shows a structural effect of the posterior phenyl group on the bond lengths and angles in coordination complexes of $[To^M]^-$, where the Tl1–N1 and Tl1–N2 distances are approximately 0.05 Å longer than the Tl1–N3 distance. This distortion is apparently related to the relative orientation of the phenyl group that is approximately perpendicular to the N3-containing oxazoline ring (torsion angle Cl7–Cl6–B1–Cl1 = 91.72°; C21–Cl6–B1–Cl1 = 81.23°) and pointing at the other two oxazoline rings (Cl7–Cl6– B1–Cl = 30.54°; C21–Cl6–B1–C6 = 38.42°). This orientation breaks the C_{3v} symmetry in the crystalline state and results in longer Tl1–N1 and Tl1–N2 distances versus Tl1–N3. Although this effect was observed in other { κ^3 -To^M}M compounds, competing steric effects of the substituents on the metal center also affect M–N bond distances, obscuring the structural impact of the phenyl group.^{21a} This posterior phenyl effect is most pronounced in **1** because the Tl center is three coordinate.

Attempts to prepare **2** from Li[To^P] and Tl[NO₃], using a modification of the procedure that provides Tl[To^M], were unsuccessful. Additionally, Tl[PF₆] and Li[To^P] or K[To^P] did not afford isolable **2**. The most efficient synthetic procedure involves reaction of Li[To^P] and Tl[OAc] in methylene chloride to provide **2** (eq 2).



We were not able to detect a cross-peak in a ${}^{1}\text{H}{-}{}^{15}\text{N}$ HMBC experiment, nor could an X-ray quality single crystal of **2** be obtained. However, a single ν_{CN} band in the infrared spectrum of **2** (1590 cm⁻¹) suggests that all three oxazolines are coordinated to the thallium center as in **1**. Additionally, the 4*S*-isopropyl-2-oxazoline groups are equivalent in the ${}^{1}\text{H}$ NMR spectrum (benzene-*d*₆). These data also indicate that the compound has not epimerized and is enantiomerically pure.

Reaction of 1 and 0.5 equiv of $[Rh(\mu-Cl)(CO)_2]_2$ provides 3 in excellent yield (eq 3).



The oxazoline groups in **3** are equivalent on the ¹H NMR time scale, as in the previously reported $To^{M}IrL_{2}$ and $To^{P}IrL_{2}$ compounds.^{12b,c} Cross-peaks in a ¹H-¹⁵N HMBC experiment provided the ¹⁵N NMR chemical shift for **3** (-163 ppm), which is upfield of noncoordinated oxazoline.

Five carbonyl bands were observed in the infrared spectrum of **3** (see Table 1). The IR bands indicate that **3** is a mixture of three isomers in which the tris(oxazolinyl)borate ligands are bi- and tridentate, and these species interconvert

^{(21) (}a) Pawlikowski, A. V.; Ellern, A.; Sadow, A. D. *Inorg. Chem.* **2009**, *48*, 8020–8029. (b) Dunne, J. F.; Manna, K.; Wiench, J. W.; Ellern, A.; Pruski, M.; Sadow, A. D. *Dalton Trans.* **2010**, *39*, 641–653.

| Table 1. Infrared Spectroscopic Data for Tris(oxazolinyl)borato Rhodium and Related Tris(pyrazolyl)borato | | | |
|---|--|--|--|
| Rhodium Carbonyls | | | |

| compound | $\nu_{\rm CO} ({\rm KBr, cm^{-1}})$ | $\nu_{\rm CN} ({\rm KBr, cm^{-1}})$ |
|---|--|---------------------------------------|
| $To^{M}Rh(CO)_{2}$ (3) | κ^2 : 2070, 2010, 1997 | noncoordinated: 1616 |
| | κ^3 : 2048, 1968 | Rh coordinated: 1571 |
| $To^{P}Rh(CO)_{2}(4)$ | κ^2 : 2072, 2002 | Rh coordinated: 1575 |
| $To^{M}Rh(CO)[P(OMe)_{3}]$ (5) | κ^{2} : 1995 | noncoordinated: 1610 |
| | κ^{3} : 1965 | Rh coordinated: 1576 |
| $[Rh{iPr-trisox}(\eta^4-C_8H_{12})][BF_4]^{14}$ | n.a. | $1644, 1643, 1623^{14}$ |
| $Tp*Rh(CO)_2^{19}$ | κ^2 : 2108, 2073 ^{19c} | n.a. |
| | κ^2 : 2083, 2012 ^{19c} | |
| | κ^3 : 2051, 1972 ^{19c} | |
| | κ^3 : 2052, 1974 ^{19a} | |
| $Tp^{Me}Rh(CO)_2^{19}$ | κ^3 : 2061, 1981 ^{19a} | n.a. |
| $Tp^{Me2Cl}Rh(CO)_2^{26}$ | κ^2 : 2083, 2017 | n.a. |
| | κ^{3} : 2059, 1984 | |
| $[{N-Me-\kappa^2-To^M}Rh(CO)_2]OTf(6)$ | 2083, 2012 | 1580, 1551 |
| $(\kappa^{3}-To^{M})Rh(\eta^{1}-C_{3}H_{5})Cl(CO)(7)$ | 2058 | 1582 |
| $(\kappa^3 - To^M)Rh(CHCl_2)Cl(CO)$ (8) | 2088 | 1575 |
| $(\kappa^3 - \text{To}^P) \hat{\text{Rh}}(\hat{\text{CHCl}}_2) \hat{\text{Cl}}(\hat{\text{CO}}) \hat{\textbf{(9)}}$ | 2092 | 1590 |
| Tp ^{Me2Cl} Rh(CHCl ₂)Cl(CO) ⁶ | 2110 ⁶ | n.a. |

rapidly on the ¹H NMR time scale. Similar mixtures of bidentate and tridentate tris(pyrazolyl)borate coordinate modes were reported for Tp*Rh(CO)₂ based on infrared analysis, ¹⁹ and these data allow a comparison of the electron-donating properties of To^M and Tp* ligands in this rhodium system. The symmetric normal modes for { κ^2 -To^M}Rh(CO)₂ (2070 cm⁻¹) and { κ^2 -Tp*}Rh(CO)₂ (2083 cm⁻¹)^{19c} suggest that the oxazolinylborate ligand is more electron donating than Tp*. Likewise, the bands for the tridentate isomer { κ^3 -To^M}Rh(CO)₂ (2048 and 1968 cm⁻¹) suggest a rhodium(I) center more electron rich than in { κ^3 -Tp*}Rh(CO)₂ (2052 and 1974 cm⁻¹). These comparisons are complicated by conformational changes in coordination modes; however the trend that [To^M] is more electron donating than Tp* is also consistent with the ν_{CO} obtained from the solution-phase IR spectra.

The presence of $\{\kappa^2\text{-}\text{To}^M\}\text{Rh}(\text{CO})_2$ in the mixture is also supported by the ν_{CN} of the oxazoline moiety. Two ν_{CN} bands were observed in the IR spectrum of **3** corresponding to coordinated (1571 cm⁻¹) and noncoordinated (1616 cm⁻¹) oxazoline rings. For comparison, the ν_{CN} band for 2*H*-4,4-dimethyl-2-oxazoline is 1630 cm⁻¹.²²

Although the carbonyl region of the infrared spectrum suggests that two or three isomers are present in **3**, ¹⁹ an X-ray diffraction study showed one { κ^2 -To^M}Rh(CO)₂ isomer (Figure 2). This { κ^2 -To^M}Rh(CO)₂ is the first crystallographically characterized neutral (i.e., nonmethylated and nonprotonated), monovalent group 9 tris(oxazolinyl)borate compound. For comparison, tris(pyrazolyl)borato rhodium(I) compounds crystallize with tridentate and/or bidentate coordination geometries.^{19,23–27} The crystallized structure contains

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Figure 2. ORTEP diagram of To^MRh(CO)₂ (**3**) drawn at 35% probability. Hydrogen atoms are not included. Bond distances (Å): Rh1-C22, 1.851(2); Rh1-C23, 1.854(2); Rh1-N1, 2.087(1); Rh1-N2, 2.096(2). Bond angles (deg): C22-Rh1-C23, 86.14(8); N1-Rh1-N2, 92.28(7); N1-Rh1-C23, 178.37(7); N2-Rh1-C22, 178.52(7). Nonbonding distances (Å): Rh1-N3, 3.43; Rh1-O3, 3.82; Rh1-C15, 3.20.

a square-planar rhodium center ($\sum_{L-Rh-L'} = 359.99^\circ$). The pendant, noncoordinated oxazoline blocks one face of the square-planar complex. That oxazoline is oriented such that its oxygen and nitrogen atoms have roughly similar distances to the rhodium center (Rh···O: 3.82 Å; Rh···N: 3.42 Å). Chelation forms a six-membered ring, and the B1-C5-N1-Rh1-N2-C10 atoms in the ring adopt a boat conformation. The pendant oxazoline is pseudoaxial, and the phenyl group is pseudoequatorial.

Reaction of **2** and 0.5 equiv of $[Rh(\mu-Cl)(CO)_2]_2$ provides **4**. As observed in **3**, the oxazoline groups are equivalent in the ¹H NMR spectrum at room temperature. The ¹⁵N NMR chemical shift (-182.8 ppm) was similar to that observed for To^PIr(CO)₂ (-184 ppm). In contrast to **3**, only two carbonyl

⁽²²⁾ Meyers, A. I.; Collington, E. W. J. Am. Chem. Soc. 1970, 92, 6676–6678.

bands were observed in the infrared spectrum with relative energies that suggest a κ^2 -To^PRh interaction.¹⁹ Strangely, only one $\nu_{\rm CN}$ band at 1575 cm⁻¹ due to coordinated oxazoline was detected; a band consistent with noncoordinated oxazoline (ca. 1630–1610 cm⁻¹) was not evident.

A related cationic chiral compound $[{\kappa^2-iPr-trisox}Rh-(\eta^4-C_8H_{12})][BF_4]$ was reported by Gade and co-workers, in which the neutral tris(oxazolinyl)ethane ligand forms a bidentate chelate with rhodium(I).¹⁴ This bidentate coordination mode is observed in an X-ray crystal structure, but several $\nu_{\rm CN}$ bands in the infrared spectrum (1664, 1643, and 1623 cm⁻¹) and equivalent oxazoline groups in the solution-phase ¹H NMR spectrum suggest that additional conformations are present. It is interesting as well that the $\nu_{\rm CN}$ bands in the cationic *i*Pr-trisox rhodium(I) are 48–89 cm⁻¹ higher in energy than the zwitterionic 4. Thus, the zwitterionic character in compound 4 likely significantly perturbs the electronic interaction between the oxazoline and the metal center.

Reactivity of To^MRh(CO)₂ (3) and To^PRh(CO)₂ (4). Oxazoline N-Methylation and Substitution Reactions. TpRh-(CO)₂ reacts with phosphines to give mixed TpRh(CO)-(PR₃).^{5,28} In the [To^M]-rhodium system, attempts to substitute one carbonyl ligand with a phosphine were not successful (PPh₃: no reaction up to 80 °C for 5 h; PMe₃: multiple products formed immediately after addition, as determined by ¹H NMR spectroscopy). However treatment of **3** with the phosphite P(OMe)₃ rapidly produces To^MRh(CO)-[P(OMe)₃] (**5**), showing that one of the carbonyl ligands can be substituted (eq 4). The three oxazolines are equivalent in the ¹H NMR spectrum at room temperature due to rapid exchange (as in **3**). Both bidentate and tridentate tris(oxazolinyl)borate binding modes are present in **5** on the basis of its observed infrared spectrum (ν_{CO} : 1995 and 1965 cm⁻¹; ν_{CN} : 1610 and 1576 cm⁻¹).



As in the single-crystal structure of **3**, the X-ray structure of **5** shown in Figure 3 contains a square-planar rhodium center ($\sum_{L-Rh-L'} = 360.2^{\circ}$). In the latter compound, the Rh–N distances are slightly longer (Rh1–N1, 2.117(2); Rh1–N3, 2.118(2) Å) than the distances in the former (Rh1– N1, 2.087(1); Rh1–N2, 2.096(2) Å). The nonbonding Rh–N distance is longer as well (3.69 Å versus 3.43 Å), and these longer distances are most likely due to steric effects. As in **3**, the six-membered chelate rings in the structure of compound **5** form the boat configuration. The relative disposition of the oxazoline methyl groups are best described by their spatial relationship with the phosphite and the carbonyl ligands.



Figure 3. ORTEP diagram of $To^{M}Rh(CO)[P(OMe)_{3}]$ (5). Hydrogen atoms are not depicted.

Specifically, the Rh1–P1 bond is coplanar with the C2–C22 bond in the oxazoline *cis* to the phosphite (torsion angle P1–Rh1–C2–C22: 1.74°); the Rh1–C26 bond is coplanar with the C9–C11 bond in the oxazoline *cis* to the carbonyl ligand (torsion angle C26–Rh1–C9–C11: 0.24°). These two oxazoline methyl groups (C22 and C11) are disposed *syn* to each other. The other two oxazoline methyl groups (C3 and C10) are pseudoaxial and are both directed toward the opposite face of the rhodium center with respect to the noncoordinated oxazoline.

Compound **3** reacts with MeOTf (3.5 equiv, methylene chloride solvent, room temperature) to give an *N*-methylated oxazoline rather than a rhodium(III) methyl complex (eq 5).



The connectivity of the N-methylated product was unambiguously identified by a ¹H-¹⁵N HMBC experiment that showed a cross-peak between a nitrogen signal at -211.0 ppm and a methyl resonance at 2.90 ppm. A crosspeak between the N-methylated oxazoline nitrogen resonance and the methylene singlet in the ${}^{1}H^{-15}N$ HMBC experiment was also observed, as expected for a C_s -symmetric compound. The chemical shift of the two equivalent rhodium-coordinated oxazolines was observed as a crosspeak at -176.7 ppm. In the ¹H NMR spectrum, three methylene signals from the oxazolines were evident as one singlet and two diastereotopic doublets. Symmetric and asymmetric v_{CO} bands were apparent in the product's infrared spectrum, and no acyl signals were visible. Furthermore, the $v_{\rm CO}$ frequencies do not change significantly from 3 after methylation, arguing against a Rh(I) to Rh(III) oxidation. A single-crystal X-ray structure, shown in Figure 4, confirmed

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Figure 4. ORTEP diagram of the cationic portion of $[{N-\text{Me-}\kappa^2-\text{To}^M}]$ Rh(CO)₂]⁺ (6). Hydrogen atoms, the OTf⁻ counteranion, and a disordered solvent molecule are not included in the representation.

that the connectivity established in solution is maintained in the solid state.

Given our previous observations with the tris(oxazolinyl)borato iridium(I) compounds $To^M Ir(CO)_2$, $To^P Ir(CO)_2$, and $To^P Ir(\eta^4-C_8H_{12})$, ¹² *N*-alkylation is not a surprising reaction pathway. However, this reactivity directly contrasts the oxidative addition reactions of Tp*RhL(CO) and MeI that give [Tp*RhMe(L)(CO)]I.⁵ Considering the oxidative addition chemistry of Tp*Rh(CO)₂ and the comparable electron richness of **3** with the Tp analogues, it is difficult to rationalize the lack of oxidative addition reactivity for either the tris(oxazolinyl)borato rhodium(I) or iridium(I) compounds. For this reason, we explored reactions of **3** with other electrophiles.

Oxidative Addition Reactions of $To^{M}Rh(CO)_{2}$ (3) and $To^{P}Rh(CO)_{2}$ (4). In contrast to the *N*-methylation reactions described above, treatment of 3 with a large excess of allyl bromide (1.9 mL) in benzene gives the oxidative addition product (κ^{3} -To^M)Rh(η^{1} -C₃H₅)Br(CO) (7) after 5 h (eq 6). A large excess is necessary, as 1, 2, and 4 equiv give mixtures of 7 and unidentified species. The crude complex was purified by recrystallization from a concentrated acetonitrile solution at -30 °C.



Oxidative addition and Rh–C bond formation to give an η^1 -C₃H₅ ligand is supported by the ¹³C{¹H} NMR spectrum that contained a resonance at 20.5 ppm (¹J_{RhC} = 16 Hz) for the σ -bonded carbon of the η^1 -allyl moiety. In contrast, Rh–C coupling was not observed in the *N*-methylated **6**. A similar spectral signature to that observed for **7** was reported for Tp*Rh(η^1 -C₃H₅)Br(NCMe) ($\delta_{RhC} = 18.0$; ¹J_{RhC} = 18 Hz).²⁹





Figure 5. Newman projection of one of two enantiomers of the racemic mixture of C_1 -symmetric (κ^3 -To^M)Rh(η^1 -C₃H₅)Br(CO) (7) viewed along the Rh–B bond. Through-space close contacts between oxazoline methyl groups and the σ -allyl ligand, detected using a NOESY experiment, are illustrated with arrows. Through-bond coupling between an oxazoline nitrogen and σ -allyl ligand is observed with a ¹H–¹⁵N HMBC experiment and is highlighted in blue.

Additionally, the ¹³C{¹H} NMR spectrum of 7 contained a single carbonyl resonance at 186.5 ppm (${}^{1}J_{RhC} = 60$ Hz). In contrast to the C_s -symmetric, N-alkylation product formed from MeOTf and 3, compound 7 is C_1 symmetric. The 4,4-dimethyl substituents on the oxazoline rings are inequivalent and provide six singlet resonances in the ¹H NMR spectrum. In a COSY experiment, the multiplet signal of the internal vinylic proton on the η^1 -allyl (6.99 ppm) correlated with the terminal vinylic resonances (doublets at 5.58 and 5.24 ppm) and with the allylic CH₂ group (4.57 and 3.64 ppm). A ¹H NOESY experiment provided evidence that these two diastereotopic allylic protons and the four methyl groups on the oxazolines are in close proximity, and therefore those oxazolines are *cis* to the η^{1} -C₃H₅ ligand. The dimethyl of the remaining oxazoline did not show through-space coupling to the σ -allyl, and this oxazoline was assigned as trans (as illustrated by the Newman projection in Figure 5). These assignments were supported by a ${}^{1}\text{H}-{}^{15}\text{N}$ HMBC experiment that showed correlations between those dimethyls (1.04 and 0.81 ppm) and the same oxazoline nitrogen (-203.5 ppm), proving that the methyl groups are on the same oxazoline ring. Cross-peaks between the other two oxazoline nitrogens (-163.5 and -187.8 ppm) and the four cis methyl groups complete the possible oxazoline assignment since CO and Br ligands are not NMR active. We also observed weak crosspeaks in the ¹H-¹⁵N HMBC experiment between the nitrogen on the *trans* oxazoline and the allylic CH₂CH=CH₂ resonances. Finally, the infrared spectrum further supports the assigned structure, as only one carbonyl band (2058 cm^{-1}) and no RhC(=O)R bands were observed.

Likewise, reaction of **3** and chloroform results in C–Cl oxidative addition rather than oxazoline alkylation (eq 7). A related thermal reaction of $Tp^{Me2Cl}Rh(CO)_2$ and chloroform affords $Tp^{Me2Cl}Rh(CHCl_2)Cl(CO)$, but $Tp*Rh(CO)_2$ and CHCl₃ do not provide a C–Cl oxidative addition product under reported thermal conditions.⁶ However, Jones has described oxidative addition reactions of $Tp*RhL_2$ (L = CNCH₂CMe₃) and CHCl₃ that occur upon photolysis, and presumably a photon mediates the Rh–L dissociation as the first step.³⁰



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Like 7, compound 8 is C_1 -symmetric. This symmetry was reflected in the ¹H NMR spectrum that contained six singlet resonances for six inequivalent methyl groups on three inequivalent oxazolines. Evidence for the structure of 8 was provided by a doublet resonance in the ¹H NMR spectrum at 7.81 ppm (${}^{2}J_{RhH} = 3.2 \text{ Hz}$) for the RhCHCl₂ moiety. A ${}^{1}\text{H}-{}^{13}\text{C}$ HMQC experiment showed a correlation between the CHCl₂ resonance and the CHCl₂ at 63.7 ppm for the rhodium carbyl (${}^{1}J_{RhC} = 26$ Hz). Through-space coupling between the CHCl2 signal and oxazoline methyl resonances was observed in a NOESY experiment, and these methyls were thus assigned to the oxazoline groups cis to the CHCl₂ ligand. A ¹H-¹⁵N HMBC experiment contained cross-peaks for the three different oxazoline nitrogens at -198.0, -187.8, and -177.6 ppm, respectively. The most upfield resonance is correlated to the oxazoline trans to the CHCl₂ group (assigned using a NOESY); in 7, the oxazoline *trans* to the allyl group is also most upfield (-203 ppm). The other two oxazoline nitrogens correlate with the methyl groups assigned as cis using data from the NOESY experiment. Unexpectedly, the ¹H-¹⁵N HMBC experiment revealed through-bond correlations between one of the cis-oxazoline nitrogens and the CHCl₂ group, while no through-bond interaction was detected with the nitrogen on the trans-oxazoline.

The oxidative addition reactions of **3** and C_3H_5Br or CHCl₃ described above provide chiral racemic products. We were therefore curious to investigate possible selectivity for the formation of diastereomers controlled by the enantiopure chiral ligand $[To^P]^-$. The reaction of **4** and chloroform gives (κ^3 -To^P)Rh(CHCl₂)Cl(CO) (**9**) (eq 8), and the major product is isolated as analytically and spectroscopically pure material after column chromatography. As the ¹H and ¹³C-{¹H} NMR spectrum demonstrated for **8**, the ¹H NMR spectrum of To^PRh(CHCl₂)Cl(CO) contained a doublet resonance due to the CHCl₂ group (7.11 ppm, ²J_{RhH} = 3.2 Hz). Doublets were also observed for the RhCHCl₂ (65.7 ppm, ¹J_{RhC} = 28.0 Hz) and the rhodium carbonyl (179.7 ppm, ¹J_{RhC} = 59.5 Hz) in the ¹³C{¹H} NMR spectrum. All three oxazoline groups are inequivalent due to the compound's overall C_1 -symmetry.



A NOESY experiment showed a cross-peak between two of the isopropyl methine hydrogens (2.37 and 2.17 ppm) with the CHCl₂ hydrogen, and these were the only hydrogen atoms for which through-space correlations with the dichlorohydrocarbyl ligand were observed. Thus, the two corresponding chiral oxazolines of the To^P ligand were assigned as *cis*; a ¹H-¹⁵N HMBC experiment allowed the detection of the *cis*oxazoline nitrogen resonances (-204.3 and -217.7 ppm). The remaining nitrogen resonance (-194.2 ppm) corresponds to an oxazoline group *trans* to the CHCl₂. As in **8**, through-bond correlations between CHCl₂ and oxazoline nitrogen were detected; in this case, cross-peaks between the CHCl₂ group and one of the *cis*-oxazolines and the *trans*-oxazoline nitrogen were observed. The through-metal coupling between *cis* ligands, in both **8** and **9**, is unexpected. Additionally, no clear trend relating

¹⁵N chemical shift to the ligand field of its *trans*-disposed ligand can be currently identified. For example, the most downfield ¹⁵N NMR chemical shift in **9** was the oxazoline nitrogen *trans* to CHCl₂, whereas the oxazoline *trans* to the dichlorohydrocarbyl ligand was the farthest upfield in **8**.

Inspection of the ¹H NMR spectrum of the crude mixture obtained from treatment of **4** in chloroform indicated that two products were formed in a 100:3 ratio. The relative ratio of the two products was determined by integration of the $CHMe_2$ signals in the ¹H NMR spectrum of the crude reaction mixture; the $CHMe_2$ and CH_2 oxazoline resonances, as well as C_6H_5 resonances, for the two species are significantly overlapping. Unfortunately, the minor product could not be isolated and fully characterized, so we tentatively assign it as the minor diastereomer on the basis of its three isopropyl methyne resonances that are indicative of a C_1 -symmetric species. No other products were observed in the crude reaction mixture.

The mechanism of oxidative addition and observed high diastereoselectivity are likely related, but unfortunately our attempts to determine a rate law for these reactions have been hindered by insufficiently separated resonances in the ¹H NMR spectra. Despite the lack of quantitative kinetic data, several qualitative mechanistic observations should be considered. First, no change in rate or selectivity is observed when the reactions are performed in the dark. This selectivity contrasts the reactions of Tp*RhL2 and CHCl3 described by Jones and co-workers, where Tp*RhCl₂ is the thermal product and Tp*Rh(CHCl₂)Cl(L) is the photochemical product.³⁰ PyboxRhCl₃ is an important side product (30%) in the reaction of pyboxRh(η^2 -C₈H₁₄) and chloroform, and this chlorinated product is attributed to oneelectron chemistry.¹⁶ Second, unlike the well-studied S_N 2type oxidative addition reactions of TpRh(CO)L and MeI, where both CO and L ligands are incorporated into the Rh(III) products,⁵ one of the carbonyl ligands dissociates during the oxidative addition reactions of both 3 and 4. Carbonyl substitution is also observed in the reaction of the rhodium(I) compound 3 and P(OMe)₃, and this transformation suggests that CO dissociation/substitution (through an associative mechanism) could occur prior to rhodium oxidation in the addition reactions. We surmise that CO is not labile in the rhodium(III) complexes because the η^1 -allyl product 7 does not decompose to $To^{M}Rh(\eta^{3}-C_{3}H_{5})Br$.

In contrast to a mechanism involving prior association of $CHCl_3$, the S_N2 -type pathway was proposed for the reaction of $Tp^{Me2Cl}Rh(CO)_2$ and $CHCl_3$ because $Tp^*Rh(CO)_2$ and $CHCl_3$ do not react under thermal conditions.⁶ We also observe differences in rate of $CHCl_3$ oxidative addition with **3** versus **4**, suggesting that these reactions do not involve radical species. Given the current mechanistic ambiguity and the product's unknown absolute stereochemistry, several models that rationalize the high diastereoselectivity could be proposed. Regardless of the pathway, however, the third oxazoline must play a significant role, either to distinguish the faces of a square-planar rhodium(I) center or to control the configuration of a five-coordinate rhodium intermediate.

Conclusion

Reactions of tris(oxazolinyl)borato rhodium(I) compounds and MeOTf proceed via *N*-oxazoline methylation, as previously reported for our related oxazolinylborato iridium(I) compounds. However, the oxidative addition

chemistry of compounds 3 and 4 has not been observed with $To^{M}IrL_{2} \text{ or } To^{P}IrL_{2} (L_{2} = (CO)_{2}, \eta^{4}-C_{8}H_{12})$. Regarding this contrast between reactive rhodium and inert iridium tris-(oxazolinyl)borates in thermal oxidative addition reactions, either higher nucleophilicity or increased carbonyl lability for the rhodium(I) compounds may be important. Although greater basicity of TpIr(CO)₂ than TpRh(CO)₂ is shown by their reactions with HBF₄·Et₂O,¹³ comparisons of kinetic parameters for oxidative addition reactions of rhodium versus iridium pyrazolylborates have not been established. Assessing the nucleophilicity of the pyrazolylborate and oxazolinylborate group 9 compounds is complicated by several factors, including multiple accessible configurations (κ^2 -boat, κ^2 -chair, and κ^3 -coordination geometries) that rapidly equilibrate and steric effects that are difficult to quantify. For example, the relative rate of reaction for chiral 4 and CHCl₃ is greater than the rate of reaction involving achiral 3; only one configuration is observed by IR spectroscopy for the former, whereas three sets of carbonyl bands are observed for the latter, and it is not clear which conformer(s) are directly involved. These structures also complicate the analysis of the electron-donating properties of tris(oxazolinyl)borate and tris(pyrazolyl)borate ligands; however the carbonyl stretching frequency of the configurationally rigid rhodium(III) series provides the trend: $(\kappa^3 - To^M)Rh(CHCl_2)$ -Cl(CO) (8; ν_{CO} : 2088 cm⁻¹) > (κ^3 -To^P)Rh(CHCl₂)Cl(CO) (9; ν_{CO} : 2092 cm⁻¹) > Tp^{Me₂Cl}Rh(CHCl₂)Cl(CO) (ν_{CO} : 2110 cm⁻¹).⁶ This trend correlates with the relative energies of carbonyl stretching frequencies for rhodium(I) dicarbonyls, but the "relative electron richness" of the rhodium center does not correlate with relative rates of reactions of [Rh] with CHCl₃. These data provide an estimate of the relative electron-donating capabilities of $[To^M]^-$ and $[To^P]^-$ ligands

to rhodium(III), as well as a basis for comparison to Cp⁻, Tp⁻, and their derivatives.

The different reaction pathways for MeOTf, allyl bromide, and chloroform substrates with 3 are readily ascribed to the electrophilicity of the RX reagent; in particular MeOTf and 2H-4,4-dimethyl-2-oxazoline react rapidly by N-methylation at room temperature, whereas chloroform and the same 2H-oxazoline do not react at 60 °C after 12 h. A second feature that distinguishes MeOTf from allyl bromide and chloroform is the relative bonding capability of OTf versus Br⁻ and Cl⁻, where halides are better coordinating ligands for rhodium than triflate. The relative binding capabilities of halides to rhodium(I) and hard electrophiles (Me^+, H^+, Li^+) to an oxazoline may also play an important part in the synthesis of oxazolinylborato rhodium compounds, such that Tl[To^M] and Tl[To^P] proved to be superior ligand transfer agents. These examples provide strategies for developing new oxidative addition reactions to better understand the effect of ancillary ligands, substrates, and reaction mechanism on stereoselectivity in organometallic chemistry.

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