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Structurally diverse Rh(I) and Mn(I) complexes derived from the new ambidentate indene ligand, (1-{^{i}Pr$_2$P(S)}-2-{NMe$_2$})C$_9$H$_6$†

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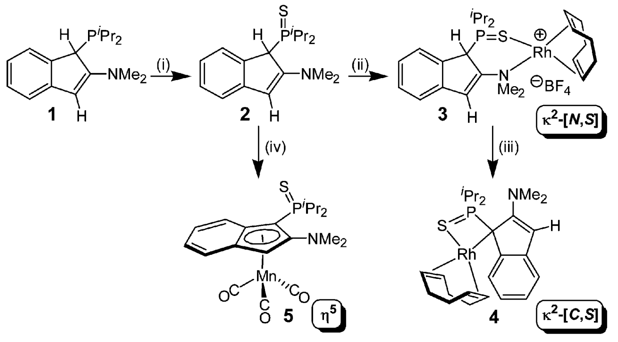
Received (in Cambridge, UK) 8th July 2004, Accepted 17th August 2004
First published as an Advance Article on the web 21st September 2004

A new indene-based ligand featuring pendant phosphine sulfide and amine donor fragments has been developed; Rh(I) coordinates to the neutral form of the ligand in a κ^2-[*N*,*S*] fashion, while the anionic form of the ligand binds Rh(I) and Mn(I) in κ^2-[*C*,*S*] and η^5 modes, respectively.

The design and synthesis of new ancillary ligands represent a persistent goal in transition metal chemistry. Such ligands provide a direct means of influencing the steric and electronic topology of the metal coordination sphere.[1] Ambidentate ligands that combine multiple chemically diverse donor fragments are particularly attractive in this regard, since they can be designed to bind a range of metal fragments, and can allow for the rational preparation of polynuclear complexes.[2] Our group is exploring the coordination chemistry of new donor-functionalized indene ligands that feature a pendant bidentate chelation site and an unsaturated carbocyclic framework for metal binding. Recently we introduced the P,N-functionalized indene **1** (Scheme 1) and demonstrated that this ligand can be used in the preparation of cationic and zwitterionic κ^2-[*P*,*N*]Rh(I) complexes that are active catalysts for C–H/Si–H dehydrogenative cross-coupling.[3] In the case of the unusual zwitterionic Rh(I) species derived from **1**, the carbocyclic backbone of the ligand functions as a sequestered, uncoordinated 10π indenide counter anion, rather than as a locale for metal binding.

Intrigued by the coordination behavior exhibited by **1**, we have initiated a study of other donor-substituted indenes, including those bearing phosphine sulfide donors. From a practical perspective, such ligands are appealing targets for use in catalytic applications since phosphine sulfides commonly exhibit increased oxygen stability relative to phosphines, while at the same time presenting a soft sulfur donor atom for binding to late transition metals.[4] Herein we report the synthesis and characterization of the new P(S),N-functionalized indene, **2**, and some preliminary coordination chemistry of this ligand with Rh(I) and Mn(I) fragments.



Scheme 1 (i) 0.125 S$_8$; (ii) 0.5 [CODRhCl]$_2$, AgBF$_4$; (iii) NaN(SiMe$_3$)$_2$; (iv) *n*-BuLi, then BrMn(CO)$_5$. Only one enantiomer of **5** is depicted.

Addition of S$_8$ to a solution of **1** resulted in the clean conversion to **2** (^{31}P NMR); following workup, **2** was isolated as an analytically pure yellow solid in 87% yield. The structural formulation provided for **2** is supported by both NMR and X-ray diffraction data.† The crystal structure of **2** is shown in Fig. 1.[5] Notably, the P–S and P–C1 distances in **2** are lengthened relative to other 1-indenylphosphine sulfides.[6,7] Treatment of **2** with [CODRh(THF)$_2$]$^+$BF$_4^-$ (prepared *in situ*) provided [(κ^2-*N*,*S*-**2**)RhCOD]$^+$BF$_4^-$ (**3**) as an analytically pure orange-red solid in 76% isolated yield (COD = η^4-(1,5-cyclooctadiene)). ^{1}H and ^{13}C NMR data indicate that the connectivity in **2** is retained upon coordination to Rh in **3**. While the NMe$_2$ fragment in **3** gives rise to a single broad ^{1}H NMR signal at 298 K, two distinct NMe resonances are observed at 223 K, in keeping with the C_1 symmetry of **3**. These observations are consistent with a dynamic process involving Rh–N dissociation, rotation about the N–C2 bond, inversion at N, and re-coordination to Rh. Analysis of variable-temperature ^{1}H NMR data yielded a value for $\Delta G^{\ddagger}_{279}$ of *ca.* 14 kcal mol^{-1} for this process. The ^{31}P{^{1}H} NMR spectrum of **3** is also temperature-dependent; at 298 K, the spectrum is comprised of a broad resonance centered at 103 ppm, while at 223 K a sharp doublet ($^2J_{\mathrm{RhP}}$ = 5 Hz) at 107 ppm is observed. The shift to high frequency of the ^{31}P NMR signal on going from **2** (73 ppm) to **3**, along with the magnitude of the Rh–P coupling constant, provides strong evidence for a Rh–S linkage in **3**.[8]

In an attempt to generate a neutral κ^2-[*N*,*S*]Rh(I) complex, the cation **3** was treated with NaN(SiMe$_3$)$_2$ and the progress of the reaction was monitored (^{31}P NMR); clean conversion to a new complex was observed (83 ppm, doublet, $^2J_{\mathrm{RhP}}$ = 14 Hz). However, analysis of NMR and X-ray diffraction data revealed this product to be the κ^2-[*C*,*S*]Rh(I) complex, **4**, which was isolated as an analytically pure yellow solid in 70% yield. The crystal structure of **4** is shown in Fig. 1,[5] and represents what appears to be the first reported Rh–C–P–S ring system,[9] as well as the first η^1-coordinated indenylrhodium[10] fragment to be crystallographically characterized. The Rh(I) center in **4** possess a square planar geometry and bonds in a nearly symmetrical fashion to the olefinic groups of the COD ligand. The Rh–C–P–S ring in **4** is nearly planar (mean deviation <0.2 Å), and the Rh–C1,[11] Rh–S,[8] and P–S[8] distances are similar to those found in other complexes. Interestingly, the P–C1 distance in **4** is contracted relative to **2**, whereas the P–S distance is elongated, suggesting partial delocalization of the anionic charge along the C–P–S unit. In the pursuit of the η^5-isomer of **4**, the ligand **2** was treated with *n*-BuLi and subsequently 0.5 equivalents of [CODRhCl]$_2$. However, **4** was again formed as the major product, along with varying amounts ($\leqslant$20%) of a new product which gave rise to a singlet at 61 ppm (^{31}P NMR). We have thus far been unable to isolate this minor product and so we cannot confirm its identity as an η^5-indenylrhodium species; however, the ^{31}P NMR shift is consistent with such a formulation (*vide infra*).

So as to explore further the possibility of **2** serving as a precursor to η^5-coordinated complexes, and given our interest in developing

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† Electronic supplementary information (ESI) available: full experimental details and crystallographic data for **2**, **4**, and **5**. See http://www.rsc.org/suppdata/cc/b4/b410328a/

DOI: 10.1039/b410328a

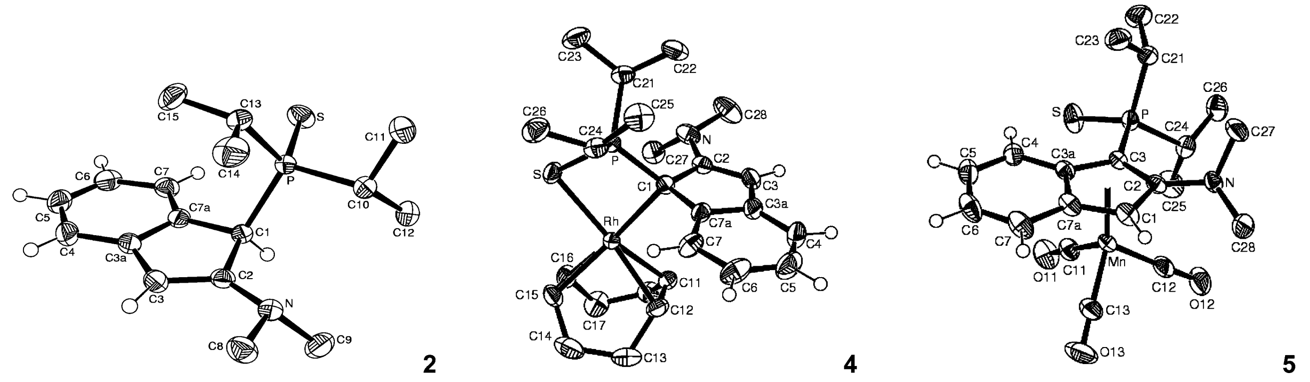

Fig. 1 ORTEP diagrams for **2**, **4**, and **5**, shown with 50% displacement ellipsoids (only one enantiomeric form is shown). Selected hydrogen atoms have been omitted for clarity. Bond lengths (Å) for **2**: P–S 1.9665(6); P–C1 1.873(2); N–C2 1.392(2); C1–C2 1.533(2); C2–C3 1.351(2). Bond lengths (Å) and angles (°) for **4**: Rh–S 2.3811(7); Rh–C1 2.233(2); Rh–C11 2.116(2); Rh–C12 2.137(3); Rh–C15 2.135(2); Rh–C16 2.153(3); P–S 2.0127(8); P–C1 1.783(2); N–C2 1.407(3); C1–C2 1.504(3); C2–C3 1.364(4); S–Rh–C1 81.07(6); Rh–C1–P 90.9(1); C1–P–S 104.30(8); P–S–Rh 81.41(3). Bond lengths (Å) for **5**: Mn–C1 2.138(2); Mn–C2 2.158(1); Mn–C3 2.131(2); Mn–C3a 2.203(2); Mn–C7a 2.190(2); P–S 1.9575(6); P–C3 1.828(1); N–C2 1.417(2).

planar-chiral, benzocymantrenyl-based ligands for use in asymmetric catalysis,[12] we turned our focus to reactions involving Mn. Lithiation of **2** followed by treatment with $BrMn(CO)_5$ led to the quantitative formation of a new phosphorus-containing product, **5** (δ ^{31}P = 64 ppm), which was isolated as an analytically pure orange solid in 96% yield. The crystallographically determined structure of **5** is given in Fig. 1,[5] and supports the solution NMR identification of this species as a half-sandwich η^5-$Mn(CO)_3$ complex lacking a Mn–S contact.[6] The $Mn(CO)_3$ fragment in **5** is distorted only modestly from ideal pentahapto coordination, unlike some other NR_2-substituted η^5-indenylmanganese complexes.[13] Particularly striking is the availability of the P(S),N chelate site in **5** to bind a reactive metal fragment. We are developing protocols for the resolution of **5**, and reports pertaining to the use of this and related complexes as chiral metalloligands in metal-mediated asymmetric transformations are forthcoming.

In summary, a new P(S),N-functionalized indene has been prepared, and preliminary reactivity studies indicate that this versatile ligand is capable of coordinating neutral and cationic metal fragments *via* κ^2-[*N*,*S*], κ^2-[*C*,*S*], and η^5 bonding modes. The synthesis and reactivity of various metal complexes supported by this and related ambidentate ligands will be the subject of future reports.

Acknowledgment is made to the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and Dalhousie University for their generous support of this work. We also thank the Atlantic Region Magnetic Resonance Centre (Dalhousie) for assistance in the acquisition of NMR data.

Notes and references

1 For selected discussions on ligand design, see: P. Comba and W. Schiek, *Coord. Chem. Rev.*, 2003, **238–239**, 21; P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Acc. Chem. Res.*, 2001, **34**, 895; D. M. Tellers, S. J. Skoog and R. G. Bergman, *Organometallics*, 2000, **19**, 2428.

2 N. Wheatley and P. Kalck, *Chem. Rev.*, 1999, **99**, 3379.

3 M. Stradiotto, J. Cipot and R. McDonald, *J. Am. Chem. Soc.*, 2003, **125**, 5618; J. Cipot, D. Wechsler, M. Stradiotto, R. McDonald and M. J. Ferguson, *Organometallics*, 2003, **22**, 5185.

4 J. C. Bayón, C. Claver and A. M. Masdeu-Bultó, *Coord. Chem. Rev.*, 1999, **193–195**, 73; T. S. Lobana, *Prog. Inorg. Chem.*, 1989, **37**, 495.

5 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565 (ORTEP3). X-Ray data for **2**, **4**, and **5** were collected at −80 °C. RM = total reflections measured; IN = independent reflections. **2**: $C_{17}H_{26}NPS$, M = 307.42, orthorhombic (*Pbca*), a = 17.316(2) Å, b = 10.834(1) Å, c = 17.787(2) Å, V = 3337.0(6) Å^3, Z = 8, μ = 0.281 mm^{-1}, RM = 22338, IN = 3424 (R_{int} = 0.0440), $R_1[F_o^2 \geqslant 2\sigma(F_o^2)]$ = 0.0338, $wR_2[F_o^2 \geqslant -3\sigma(F_o^2)]$ = 0.0887. CCDC 244733. **4**: $C_{25}H_{37}NPRhS$, M = 517.50, monoclinic ($P2_1/c$), a = 10.1379(7) Å, b = 12.4282(8) Å, c = 18.848(1) Å, β = 93.763(1) °, V = 2369.6(3) Å^3, Z = 4, μ = 0.888 mm^{-1}, RM = 15830, IN = 4830 (R_{int} = 0.0314), $R_1[F_o^2 \geqslant 2\sigma(F_o^2)]$ = 0.0281, $wR_2[F_o^2 \geqslant -3\sigma(F_o^2)]$ = 0.0770. CCDC 244734. **5**: $C_{20}H_{25}MnNO_3PS$, M = 445.38, monoclinic ($P2_1/c$), a = 9.688(2) Å, b = 15.570(4) Å, c = 13.898(3) Å, β = 91.494(4) °, V = 2095.8(8) Å^3, Z = 4, μ = 0.825 mm^{-1}, RM = 16327, IN = 4273 (R_{int} = 0.0252), $R_1[F_o^2 \geqslant 2\sigma(F_o^2)]$ = 0.0273, $wR_2[F_o^2 \geqslant -3\sigma(F_o^2)]$ = 0.0764. CCDC 244735. See http://www.rsc.org/suppdata/cc/b4/b410328a/ for crystallographic data in .cif or other electronic format.

6 M. Stradiotto, C. Kozak and M. J. McGlinchey, *J. Organomet. Chem.*, 1998, **564**, 101.

7 C. Lensink and G. J. Gainsford, *Aust. J. Chem.*, 1998, **51**, 667.

8 J. Browning, G. W. Bushnell, K. R. Dixon and R. W. Hilts, *J. Organomet. Chem.*, 1992, **434**, 241; C. Claver, A. Ruiz, A. M. Masdeu, J. Viñas, T. Saballs, F. J. Lahoz and F. J. Plou, *J. Organomet. Chem.*, 1989, **373**, 269.

9 For related M–C–P–S rings, see: M. W. Avis, M. Goosen, C. J. Elsevier, N. Veldman, H. Kooijman and A. L. Spek, *Inorg. Chim. Acta*, 1997, **264**, 43; H. H. Murray, G. Garzón, R. G. Raptis, A. M. Mazany, L. C. Porter and J. P. Fackler, Jr., *Inorg. Chem.*, 1988, **27**, 836 and references cited therein.

10 M. Stradiotto and M. J. McGlinchey, *Coord. Chem. Rev.*, 2001, **219–221**, 311 and references cited therein.

11 H. Schumann, O. Stenzel, S. Dechert, F. Girgsdies, J. Blum, D. Gelman and R. L. Halterman, *Eur. J. Inorg. Chem.*, 2002, 211; K. C. Rupert, C. C. Liu, T. T. Nguyen, M. A. Whitener and J. R. Sowa, Jr., *Organometallics*, 2002, **21**, 144.

12 For chiral cymantrenyl ligands, see: S. U. Son, K. H. Park, S. J. Lee, Y. K. Chung and D. A. Sweigart, *Chem. Commun.*, 2001, 1290; S. Kudis and G. Helmchen, *Angew. Chem., Int. Ed.*, 1998, **37**, 3047.

13 H. Plenio and D. Burth, *Organometallics*, 1996, **15**, 1151; H. Plenio and D. Burth, *Z. Anorg. Allg. Chem.*, 1996, **622**, 225.