Organometallics **1997,** *16,* 4517−4518 4517

Synthesis and Catalytic Application of $[Rh(PPh_3)_2([9]aneS_3)]PF_6$‡

Anthony F. Hill* and James D. E. T. Wilton-Ely

Department of Chemistry, Imperial College of Science Technology and Medicine,
South Kensington, London SW7 2AY, U.K.

Received July 8, 1997⊗

Summary: The reaction of $[RhCl(PPh_3)_3]$ with $[9]aneS_3$ (1,4,7-trithiacyclononane) and NH_4PF_6 provides $[Rh(PPh_3)_2([9]aneS_3)]PF_6$, which undergoes ligand substitution and oxidative-addition reactions and effectively catalyzes the demercuration of bis(alkynyl)mercurials.

The application of polythiamacrocycles (‘thiacrowns’) as co-ligands for metal-based catalysis has been mooted as grounds for the study of their coordination chemistry.[1] This rationale appreciates (i) that thiacrowns overcome the comparatively weak coordinating ability of acyclic thioethers and (ii) that thioethers may in part mimic phosphines, the catalytic utility of which is enormous. Despite the substantial growth in the coordination chemistry of thiacrowns,[2] the application of such complexes to catalysis has received scant attention, with the elegant exception of studies by Kellog who showed that Grignard cross-coupling reactions could be effected by the addition of thiacrowns to nickel chloride and that the process could be made enantioselective by employing chiral thiacrowns.[3] Although the nickel complexes involved were not identified, nickel chloride in the presence of $[14]aneS_4$ achieved yields comparable to those of triphenylphosphine while dibutyl sulfide and the acyclic thioether 2,5,9,12-tetrathiatridecane provided considerably reduced yields. More recently, Adams has shown numerous examples of the catalytic synthesis of thiacrowns from metal-mediated ring-opening oligomerizations of thietanes, which clearly involve thiacrown complex intermediates.[4]

We have been concerned recently with the preparation of organometallic complexes of thiacrowns, with a focus on investigating the compatability of such macrocycles with typical ‘C_1’ ligands involved in conventional catalytic cycles. These have included σ-vinyl, aryl, carbonyl, and thiocarbonyl ligands,[5] and we have shown that coordination of such macrocycles can induce ligand-coupling reactions.[6] We report herein the synthesis of a thiacrown complex of rhodium(I), its ligand substitution and oxidative-addition chemistry, and its deployment in a catalytic process, viz the demercuration of bis(alkynyl)mercurials to form the corresponding 1,3-diynes.[7]

Wilkinson’s catalyst $[RhCl(PPh_3)_3]$ (**1**) is unique in its versatility. This may be traced to facile interconversion between complexes of different coordination number and the accessibility of both mono- and trivalent rhodium. The reaction of (**1**) with 1,4,7-trithiacyclononane ($[9]aneS_3$) and NH_4PF_6 provides high yields of the salt $[Rh(PPh_3)_2([9]aneS_3)]PF_6$ (**2**)[8] (Scheme 1). A related series of complexes $[RhL_2([9]aneS_3)]^+$ ($L_2 = (C_2H_4)_2$, $(PPh_3)(CO)$; cod = 1,4-cyclooctadiene) has been described by Schröder,[9] and crystallographic studies indicate that the $[9]aneS_3$ macrocycle adopts a tridentate coordination mode, at least in the solid state. Spectroscopic data for **2** also support such a coordination. Given the preva-

---

* Author to whom correspondence should be addressed. Email: a.hill@ic.ac.uk.

‡ Dedicated to Dr. R. M. Scrowston in gratitude for his encouragement and guidance.

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1997.

(1) For a general review on thiacrown complexes see: Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1.

(2) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1.

(3) Kellogg, R. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 782. Vriesema, B. K.; Lemaire, M.; Butler, J.; Kellogg, R. M. *J. Org. Chem.* **1986**, *51*, 5169.

(4) Adams, R. D.; Falloon, S. B. *Chem. Rev.* **1995**, *95*, 2587.

(5) Cannadine, J. C.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1996**, *15*, 5409. Hector, A. L.; Hill, A. F. *Inorg. Chem.* **1995**, *34*, 3797. Alcock, N. W.; Cannadine, J. C.; Clark, G. R.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1993**, 1131. Hill, A. F.; Alcock, N. W.; Cannadine, J.; Clark, G. R. *J. Organomet. Chem.* **1992**, *426*, C40.

(6) Cannadine, J. C.; Hector, A. L.; Hill, A. F. *Organometallics* **1992**, *11*, 2323.

(7) Bedford, R. B.; Hill, A. F.; Thompsett, A. R.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1996**, 1059.

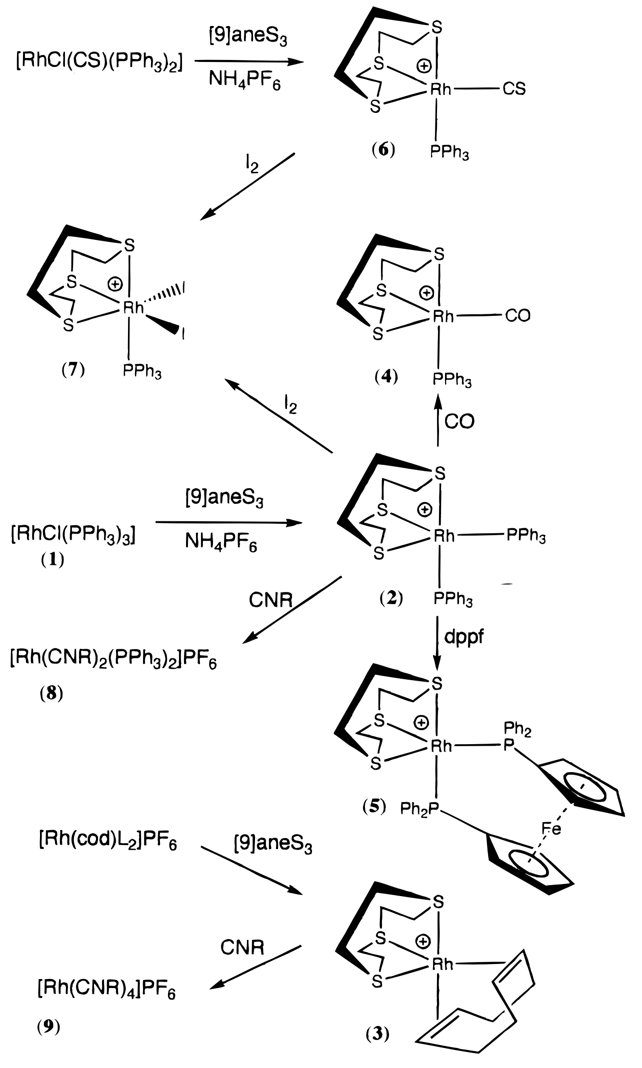
(8) Selected data for representative new complexes (25 °C, NMR ($CDCl_3$ or $CDCl_3{:}CH_2Cl_2 = 1{:}3$)). **2**: Yield 93%; ^1H NMR δ 1.88−1.97, 2.31−2.39 (m × 2, 12 H, SCH_2), 7.18−7.45 (m, 30 H, C_6H_5); $^{31}P\{^1H\}$ NMR 42.4 ppm ($^1J(RhP) = 169.6$ Hz); FAB-MS *m/z* 807 (100, $[M]^+$), 627 (32, $[M - [9]aneS_3]^+$), 545 (74, $[M - PPh_3]^+$). Anal. Calcd for $C_{42}H_{42}F_6P_3RhS_3$: C, 53.0; H, 4.4. Found: C, 52.8; H, 4.2. NB: Schröder has reported that the reaction of $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$ with 1 equiv of PPh_3 (!) and 2 equiv of $[9]aneS_3$ provides an inseparable mixture of compounds, the mass spectrum of which includes a peak at m/z = 807.[9c] **4**: Yield 81%; IR (Nujol) 1947 cm^{-1} ($\nu(CO)$); ^1H NMR δ 2.31−2.56, 2.63−2.87 (m × 2, 12 H, SCH_2), 7.41−7.79 (m × 2, 15 H, C_6H_5); $^{31}P\{^1H\}$ NMR 42.8 ppm ($J(RhP) = 128.9$ Hz), see also ref 9. **5**: Yield 63%; ^1H NMR Insufficiently soluble; $^{31}P\{^1H\}$ NMR 38.7 ppm ($^1J(RhP) = 195.8$ Hz); FAB-MS *m/z* 836 (56, $[M]^+$), 657 (12, $[M - [9]aneS_3]^+$). Anal. Calcd for $C_{40}H_{40}F_6FeP_3RhS_3$: C, 46.1; H, 4.0. Found: C, 45.5; H, 3.9. **6**: IR (Nujol) 1279 cm^{-1} ($\nu(CS)$). ^1H NMR δ 2.38−2.52, 2.76−2.90 (m × 2, 12 H, SCH_2), 7.42−7.55, 7.73−8.81 (m × 2, 15 H, C_6H_5); $^{13}C\{^1H\}$ NMR 293.0 (dd, RhCS, $^2J(PC) = 17.8$, $^1J(RhC) = 71.4$ Hz), 135.5−127.6 (C_6H_5), 36.4, 34.3, 32.2 (SCH_2); $^{31}P\{^1H\}$ NMR 43.3 ppm ($^1J(RhP) = 149.2$ Hz); FAB-MS *m/z* 1276 (1.5, $[M_2ClO_4]^+$), 742 (0.5, $[M + nba]^+$), 589 (100, $[M]^+$), 545 (4, $[M - CS]^+$). Anal. Calcd for $C_{25}H_{27}ClO_4PRhS_4{\cdot}1.25CH_2Cl_2$: C, 39.7; H, 3.7. Found: 39.7; H, 3.6. CH_2Cl_2 solvate confirmed by ^1H NMR integration. **7**: Yield 67%; ^1H NMR δ 1.22, 1.75, 2.44, 2.88, 3.72 (m × 5, 12 H, SCH_2), 7.40−7.81 (m × 2, 15 H, C_6H_5). $^{31}P\{^1H\}$ NMR 43.2 ppm ($^1J(RhP) = 149.2$ Hz); FAB-MS *m/z* 798 (7, $[M]^+$), 671 (13, $[M - I]^+$), 545 (3, $[M - I_2]^+$). Anal. Calcd for $C_{24}H_{27}ClI_2O_4PRhS_3{\cdot}1.5CH_2Cl_2$: C, 29.9; H, 3.0. Found: C, 29.8; H, 4.0. CH_2Cl_2 solvate confirmed by ^1H NMR integration. **8a**: Yield 93%; IR (Nujol) 2152, 2113 (sh) cm^{-1} ($\nu(CN)$). ^1H NMR δ 1.03 (s, 18 H, CH_3), 7.36−7.47 (m, 30 H, C_6H_5); $^{31}P\{^1H\}$ NMR 30.8 ppm; FAB-MS *m/z* 793 (100, $[M]^+$), 710 (15, $[M - CNR]^+$), 627 (12, $[M - 2CNR]^+$), 531 ($M - PPh_3]^+$). Anal. Calcd for $C_{54}H_{48}F_6N_2P_3$: C, 62.7; H, 4.7; N, 2.7. Found: C, 62.9; H, 4.8; N, 2.7. **8b**: Yield 90%; IR (Nujol) 2129 cm^{-1}($\nu(CN)$). ^1H NMR δ 1.61 (s, 12 H, CH_3), 6.84 (d, 4 H, $H^{3,5}(C_6H_3)$), 7.00 (t, 2 H, $H^4(C_6H_3)$), 7.32, 7.64 (m × 2, 30 H, C_6H_5); $^{31}P\{^1H\}$ NMR 31.2 ppm ($^1J(RhP) = 124.1$ Hz); FAB-MS *m/z* 889 (100, $[M]^+$), 758 (14, $[M - CNR]^+$), 627 (23, $[M - 2CNR]^+$), 496 (18, $[M - PPh_3 - CNR]^+$). **9**: IR (Nujol) 2165 cm^{-1}($\nu(CN)$). ^1H NMR 1.51 (s, 36 H, CH_3); FAB-MS *m/z* 435 (100, $[M]^+$), 352 (5, $[M - CNR]^+$), 266 (4, $[M - 2CNR]^+$), 184 (5, $[M - 3CNR]^+$). See also ref 10 for alternative synthesis.

(9) (a) Blake, A. J.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1991**, 253. (b) Blake, A. J.; Halcrow, M. A.; Schröder, M. *Acta Crystallogr., Sect. C,* **1993**, *49*, 85. (c) Blake, A. J.; Gould, R. O.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2197.

(10) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II *Inorg. Chem.* **1978**, *17*, 829.

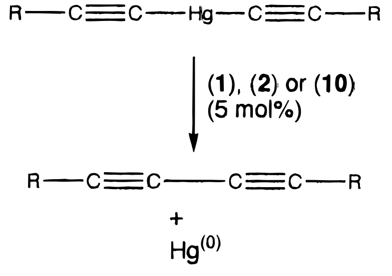
S0276-7333(97)00578-5 CCC: $14.00

Scheme 1[a]



[a] R = tBu, $\mathrm{C_6H_3Me_2}$-2,6; dppf = 1,1′-bis(diphenylphosphino)ferrocene; L = $\mathrm{PPh_3}$.

Scheme 2[a]



[a] R = $\mathrm{C_6H_4Me}$-4.

lence for four-coordinate square-planar geometries for d^8 complexes, the possibility of variable and reduced denticity should not, however, be disregarded in subsequent reactions. Surprisingly, attempts to prepare **2** from the reaction of $\mathrm{[Rh(cod)(PPh_3)_2]PF_6}$ led to phosphine rather than diene displacement and the formation of $\mathrm{[Rh(cod)([9]aneS_3)]PF_6}$ (**3**). This salt has been prepared previously *via* the reaction of $\mathrm{[9]aneS_3}$ with $\mathrm{[Rh_2(\mu\text{-}Cl)_2(cod)_4]}$.[9] Complex **2** is labile with respect to ligand substitution, e.g., carbonylation at room temperature provides the known salt $\mathrm{[Rh(CO)(PPh_3)([9]aneS_3)]PF_6}$ (**4**). The related and sparingly soluble salt $\mathrm{[Rh(dppf)([9]aneS_3)]PF_6}$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene, **5**) results from reaction of **2** with dppf.

The reaction of **2** with carbon disulfide provides $\mathrm{[Rh(\eta^2\text{-}SCS)(PPh_3)([9]aneS_3)]PF_6}$ rather than the thiocarbonyl analogue of **4**. The salt $\mathrm{[Rh(CS)(PPh_3)([9]aneS_3)]ClO_4}$ (**6**) may, however, be obtained in good yield from the reaction of $\mathrm{[RhCl(CS)(PPh_3)_2]}$ with $\mathrm{[9]aneS_3}$ and $\mathrm{NaClO_4}$ (Scheme 1).[8] Somewhat suprisingly, the thiocarbonyl ligand is cleaved from **6** by iodine to provide $\mathrm{[RhI_2(PPh_3)([9]aneS_3)]PF_6}$ (**7**). Attempts to prepare the isonitrile analogue of **4** were, however, unsuccessful: Treating **2** with pivaloisonitrile or 2-xylylisonitrile provided the salts $\mathrm{[Ru(CNR)_2(PPh_3)_2]PF_6}$ (R = tBu (**8a**), $\mathrm{C_6H_3Me_2}$-2,6 (**8b**)), while treating **3** with pivaloisonitrile leads to loss of both cyclooctadiene and the macrocycle to provide $\mathrm{[Rh(CN}t\mathrm{Bu)_4]PF_6}$ (**9**). This lability of the thiacrown is somewhat surprising. Complex **2** is also prone to oxidative addition: reaction with iodine results in the formation of the octahedral complex $\mathrm{[RhI_2(PPh_3)([9]aneS_3)]PF_6}$ (**7**).

The complex has been shown above to demonstrate two useful properties for a catalyst: facile ligand substitution and the ready accessibility of two interchangeable oxidation states. We have, therefore, investigated the suitability of **2** for a catalytic process which has recently attracted our attention.[7] We have shown that the complexes $\mathrm{[RhCl(CO)(PPh_3)_2]}$ (**10**) and $\mathrm{[OsHCl(CO)(PPh_3)_3]}$ catalyze the demercuration of bis(alkynyl)mercurials (Scheme 2).[7] In the case of **10** a mechanism has been proposed involving oxidative addition of a mercury acetylide bond, extrusion of elemental mercury from the Rh−Hg−C≡ group, and reductive elimination of the diyne from the resulting *cis*-bis(alkynyl) intermediate. Thus, this process is particularly convenient for assessing catalytic activity in that it requires oxidative-addition and reductive-elimination steps and its ensuite is immediately visible by virtue of the deposition of elemental mercury. Bis(4-tolylethynyl)mercury (1.2 mmol) was treated with 5 mol % of metal catalyst as a point of reference. We find that as previously reported, **10** effects demercuration over 2 h in refluxing tetrahydrofuran in 75% yield. Wilkinson's catalyst (**1**) achieves a comparable yield (82%), offering the trade-off of higher activity (proceeds at room temperature) against the required use of anerobic conditions. Gratifyingly, we find that **2** effects demercuration in 94% yield over 2 h in refluxing thf. Furthermore, when the reaction is run for 1 h with 15 mol % of **2**, the ^{31}P NMR spectrum of the product mixture reveals **2** to be the only organometallic complex present, indicating that **2** is a true catalyst and not merely a precatalyst. Thus, not only has a catalytic process based on a well-defined thiacrown complex been illustrated for the first time, the yields are found to exceed those for more conventional catalysts **1** and **10**. We are now investigating the deployment of **2** and its derivatives in more classical metal-mediated catalytic processes and will report subsequently.

Acknowledgment. We wish to thank the Engineering and Physical Sciences Research Council (U.K.) for the award of a studentship (to J.D.E.T.W.-E.) and Leverhulme Trust and the Royal Society for the award of a Senior Research Fellowship (to A.F.H.).

Supporting Information Available: Text giving details of the syntheses and characterization data for the complexes prepared in this paper (3 pages). Ordering information is given on any current masthead page.

OM970578Q