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A Novel Route to Dinuclear Heteroleptic Rhodium(III) Complexes of 1,4,7-Trithiacyclononane

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New mono- and dinuclear Rh(III) complex cations of 1,4,7-trithiacyclononane (9S3), $[Rh(9S3)(PPh_3)(I)_2]^+$ and $[(9S3)Rh(\mu\text{-}SPh)_3MCp^*]^{2+}$ (M = Rh, Ir; $Cp^* = C_5(CH_3)_5$), were prepared from the set of reaction systems utilizing $[Rh(9S3)(CO)(PPh_3)]^+$ (**1**) as a synthon. Oxidative decarbonylation reaction of **1** with I_2 in CH_2Cl_2 gave the mononuclear diiodo cation as a perchlorate salt in good yield. In the presence of excess benzenethiol and NEt_3, $[Rh(9S3)(PPh_3)(I)_2]^+$ (**2**) in CH_3CN undergoes substitution reaction, resulting in the formation of red insoluble neutral species **3** with the empirical formula of $Rh(9S3)(SPh)_3 \cdot CH_3CN$. Treatment of **3** with $[Cp^*MCl_2]_2$ (M = Rh, Ir)/$AgClO_4$ in CH_3CN afforded the above mentioned dinuclear cations. The compounds $\mathbf{2}ClO_4$ (**A**) and $[(9S3)Rh(\mu\text{-}SPh)_3IrCp^*](ClO_4)_2 \cdot 0.5CH_3CN \cdot 0.5CH_2Cl$ (**B**) were characterized by single-crystal X-ray diffraction studies. The compound **A** [**B**] crystallizes in the monoclinic space group $P2_1/a$ [$P2_1/n$] with a = 15.416(3) [24.554(5)] Å, b = 13.440(1) [15.706(2)] Å, c = 13.987(2) [11.725(1)] Å, β = 91.14(1) [98.36(2)] deg, V = 2897.4 [4473.6] Å^3, Z = 4 [4], D_c = 2.05 [1.78] g cm^{-3}. Data were collected on an Enraf-Nonius CAD4 diffractometer, using Mo Kα radiation, to maximum 2θ = 48 [46] deg, giving 3850 [4669] unique reflections, and the structures were solved by heavy atom method for **A** [**B**]. The final discrepancy indices for **A** [**B**] were R (R_w) = 0.038 (0.030) [0.067 (0.059)] for 3432 [2591] independent reflections with $F > 6\sigma(F)$. The cation structures of **A** and **B** reveal the endo-tridentate ligating nature of 9S3 to Rh with varying Rh−S distances. Compound **A** adopts a cis geometry for two iodide groups around the octahedral Rh center. In the cation of **B**, a $(Cp^*Ir)^{2+}$ moiety interacts with the $Rh(9S3)(SPh)_3$ unit, a unit suggested in **3**, via three μ-SPh bridges, forming a heterodinuclear species with Ir··Rh interatomic distance of 3.244 Å.

Introduction

Among crown thioethers, 1,4,7-trithiacyclononane (abbreviated 9S3) has been successfully utilized in developing the crown thioether chemistry due to its remarkable ligating nature that stems from the unique σ-donor and π-acid character and the tendency of retaining endodentate conformation on binding to a trigonal face of a metal.[1,2] The exploratory research efforts on the coordination chemistry of 9S3 have led to the determination of its scope, and this has yielded the initial preparation of a large set of homoleptic complexes of lower oxidation state transition metal ions[1−5] and p-block metal ions[6] which was followed by emergence of a new class of heteroleptic 9S3 complexes in the form of metal carbonyls,[7] metal halides,[8] metal hydrides,[9] metal oxides,[10] metal phosphines,[11] or organometallic compounds.[12]

In spite of the observation of large body of 9S3 complexes, the reports on the reactivity of 9S3 complexes[13−15] and on the synthesis of dinuclear 9S3 systems[15] and 9S3 complexes of Rh-

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(1) (a) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1. (b) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141.

(2) (a) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1. (b) Schröder, M. *Pure Appl. Chem.* **1988**, *60*, 517.

(3) (a) Blake, A. J.; Gould, R. O.; Halcrow, M. A.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1992**, 3427. (b) Bell, M. N.; Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3841. (c) Blake, A. J.; Greig, J. A.; Holder, A. J.; Hyde, T. I.; Taylor, A.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 197. (d) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1433. (e) Blake, A. J.; Gould, R. O.; Greig, J. A.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1989**, 876. (f) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schröder, M. *Polyhedron* **1989**, *8*, 2041.

(4) (a) White, D. J.; Küppers, H.-J.; Edwards, A. J.; Watkin, D. J.; Cooper, S. R. *Inorg. Chem.* **1992**, *31*, 5351. (b) Blower, P. J.; Clarkson, J. A.; Rawle, S. C.; Hartman, J. R.; Wolf, R. E., Jr.; Yagbasan, R.; Bott, S. G.; Cooper, S. R. *Inorg. Chem.* **1989**, *28*, 4040. (c) Clarkson, J. A.; Yagbasan, R.; Blower, P. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1244.

(5) (a) Setzer, W. N.; Guo, Q.; Grant, G. J.; Hubbard, J. L.; Glass, R. S.; VanDerveer, D. G. *Heteroatom Chem.* **1990**, *1*, 317. (b) Grant, G. J.; Mauldin, P. L.; Setzer, W. N. *J. Chem. Educ.* **1991**, *68*, 605.

(6) Blake, A. J.; Greig, J. A.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1991**, 529.

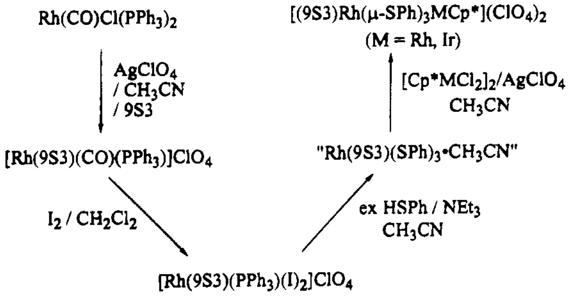
(7) (a) Kim, H.-J.; Do, Y.; Lee, H. W.; Jeong, J. H.; Sohn, Y. S. *Bull. Kor. Chem. Soc.* **1991**, *12*, 257. (b) Elias, H.; Schmidt, G.; Küppers, H.-J.; Saher, M.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 3021. (c) Pomp, C.; Drueke, S.; Küppers, H.-J.; Wieghardt, K.; Kruger, C.; Weiss, J.; Nuber, B. *Z. Naturforsch.* **1988**, *43B*, 299. (d) Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636.

(8) (a) Willey, G. R.; Jarvis, A.; Palin, J.; Errington, W. *J. Chem. Soc., Dalton Trans.* **1994**, 255. (b) Alcock, N. W.; Cannadine, J. C.; Clark, G. R.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1993**, 1131. (c) Shen, J.; Pickardt, J. *Z. Naturforsch.* **1992**, *47B*, 1736. (d) Willey, G. R.; Lakin, M. T.; Ravindran, M.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1991**, 271. (e) Reference 4b of this paper. (f) Parker, D.; Roy, P. S.; Ferguson, G.; Hunt, M. M. *Inorg. Chim. Acta* **1989**, *155*, 227. (g) Küppers, H.-J.; Wieghardt, K. *Polyhedron* **1989**, *8*, 1770. (h) Küppers, H.-J.; Wieghardt, K.; Tsay, Y. H.; Kruger, C.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 575. (i) Wieghardt, K.; Kleine-Boymann, M.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1654. (j) Wieghardt, K.; Küppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067.

(9) (a) Bell, M. N.; Blake, A. J.; Christie, R. M.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M.; Yellowless, L. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2977. (b) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1759.

0020-1669/95/1334-0796$09.00/0

Scheme 1



(III)[12d,16] are very scarce. Deprotonation and ring-opening reactivities of coordinated 9S3 are interesting, but they are of limited use in producing 9S3 derivatives.[13] Furthermore, in contrast to the expectation, the heteroleptic ligands in the heteroleptic class are not potentially susceptible for further derivative reactions and are seen as "innocent ligands"[1-12] although some use of heteroleptic 9S3 complexes has been realized in the direction of developing[14] the organometallic chemistry of ruthenium complexes bearing 9S3 as well as in the synthesis[15] of polynuclear $[RuCl(PPh_3)(9S3)]_2^{2+}$ and $[TlCl_2Ru(PPh_3)(9S3)]_2^{2+}$ ions. As part of our investigation into the extended use of heteroleptic crown thioether complexes, the monocationic Rh(I) compound $[Rh(9S3)(CO)(PPh_3)](ClO_4)]$[12d] was successfully employed to devise a systematic entry, outlined in Scheme 1, to dinuclear heteroleptic Rh(III) complexes of 9S3. Here we report detailed accounts of the synthesis, characterization, and properties of unprecedented Rh(III) complexes containing 9S3.

Experimental Section

Preparation of Compounds. All manipulations were carried out under pure dinitrogen atmosphere using a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri-Train gas purifier or a vacuum line using standard Schlenk techniques.[17] Reagent grade solvents were distilled from appropriate drying agents[18] and degassed prior to use. The deuterated solvents were dried before use by trap-to-trap distillation from the activated molecular sieves 3A. 9S3 was prepared by the literature procedure[19] or purchased from Aldrich. The chemicals $RhCl_3\cdot 3H_2O$ and $IrCl_3\cdot 3H_2O$ from Degussa, anhydrous silver perchlorate from Strem, pentamethylcyclopentadiene (Cp*H) from Kanto Chemical Co., and triphenylphosphine, silver perchlorate hydrate, benzenethiol, iodine, and triethylamine from Aldrich were purchased and used as received. $Rh(CO)Cl(PPh_3)_2$[20] and $[Cp^*MCl_2]_2$ (M = Rh, Ir)[21] were prepared according to the literature procedures.

Caution! Although the perchlorate salts described in this papers do not appear to be sensitive to shock or heat, these materials like all perchlorates should be prepared only by in small quantities.

$[Rh(CO)(PPh_3)(9S3)]ClO_4$ (1ClO4).[22] To a solid mixture of $Rh(CO)Cl(PPh_3)_2$ (438 mg, 0.63 mmol) and $AgClO_4\cdot H_2O$ (150 mg, 0.67 mmol) was added 30 mL of CH_3CN, causing instantaneous formation of a white solid. The resulting slurry was stirred for 1.5 h and filtered. The yellow filtrate was treated with solid 9S3 (120 mg, 0.67 mol). Additional stirring for 12 h gave a yellow orange solution which was then filtered. Addition of an excess amount of Et_2O to the resulting filtrate followed by cooling at −10 °C for 1 day afforded a yellow-orange crystalline product in a yield of 62% (266 mg). IR (KBr): 1957 (ν_{CO}), 1480, 1435, 1410, 1087, 902, 818, 749, 695, 622, 537, 512, 500 cm^{-1}. ^1H-NMR (DMSO-d_6): δ 2.42–2.74 (m, 12 H, 9S3), 7.54–7.72 (m, 15 H, PPh_3). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 34.61 (9S3), 129.60 (d, J = 10.7 Hz), 132.20 (s), 134.68 (d, J = 11.5 Hz) (PPh_3). A signal due to the carbonyl group was not detected. $^{31}P\{^1H\}$-NMR (DMSO-d_6): δ 42.35 (d, $^1J_{Rh-P}$ = 128 Hz).

$[Rh(9S3)(PPh_3)(I)_2]ClO_4$ (2ClO4). To a solid mixture of 1ClO4 (266 mg, 0.40 mmol) and a slight excess amount of I_2 (120 mg, 0.47 mmol) was slowly added 20 mL of CH_2Cl_2. Immediate evolution of gas presumably CO was accompanied with the precipitation of a red brown solid. The reaction mixture was stirred for 18 h and filtered to collect the red crystalline solid which was washed with cold CH_2Cl_2 and Et_2O and dried *in vacuo*. The solid was redissolved in 100 mL of CH_3CN to remove a dark solid which is insoluble in common organic solvents and filtered. Slow diffusion of Et_2O into the deep red filtrate afforded red crystals in a yield of 75% (266 mg). Anal. Calcd for $C_{24}H_{27}ClI_2O_4PS_3Rh$: C, 32.07; H, 3.03. Found: C, 32.51; H, 3.17. IR (KBr): 1480, 1433, 1411, 1078, 910, 821, 745, 694, 623, 524, 511, 480 cm^{-1}. ^1H-NMR (CD_3CN): δ 2.52–2.60 (m, 2 H, 9S3), 2.72–2.74 (m, 2 H, 9S3), 2.92–3.01 (m, 2 H, 9S3), 3.33–3.45 (m, 4 H, 9S3), 3.79–3.80 (m, 2 H, 9S3), 7.44–7.86 (m, 15 H, PPh_3). $^{31}P\{^1H\}$-NMR (CD_3CN): δ 20.30 (d, J_{Rh-P} = 96 Hz).

Rh(III)/9S3/Thiolate Compound with the Empirical Formula of $Rh(9S3)(SPh)_3\cdot CH_3CN$ (3). The addition of an excess amount of benzenethiol and NEt_3 to a solution of 2ClO4 (48 mg, 0.053 mmol) in CH_3CN led to the immediate formation of a red solid. The resulting reaction mixture was stirred for 2 days. The red solid product was collected, washed with Et_2O, and dried under N_2 stream. The insolubility of the product in most common solvents hampered its full characterization. The yield was 75% (26 mg) based on the empirical formula established by elemental analysis. Anal. Calcd for $C_{24}H_{27}S_6Rh\cdot CH_3CN$: C, 47.91; H, 4.64; N, 2.14. Found: C, 46.93; H, 5.01; N, 1.82. IR (KBr): 3042, 2967, 2913, 1572, 1462, 1446, 1431, 1400, 1077, 1062, 1022, 902, 818, 741, 694, 490 cm^{-1}.

$[(9S3)Rh(\mu\text{-}SPh)_3RhCp^*](ClO_4)_2\cdot CH_3CN\cdot CH_2Cl_2$. The reaction system generated by the addition of 15 mL of CH_3CN into a solid mixture of $[Cp^*RhCl_2]_2$ (41 mg, 0.07 mmol) and 4 equiv of $AgClO_4\cdot H_2O$ (61 mg) was stirred for 1.5 h and filtered. The yellow filtrate was added to 85 mg (0.13 mmol) of solid 3. Development of a red solution

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(10) (a) Hermann, W. A.; Roesky, P. W.; Kühn, F. E.; Scherer, W.; Kleine, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1714. (b) Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1991**, 1414. (c) Küppers, H.-J.; Nuber, B.; Weiss, J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1990**, 979.

(11) Blake, A. J.; Gould, R. O.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2909.

(12) (a) Blake, A. J.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1631. (b) Bennett, M. A.; Canty, A. J.; Felixberger, J. K.; Rendina, L. M.; Sunderland, C.; Willis, A. C. *Inorg. Chem.* **1993**, *32*, 1951. (c) Blake, A. J.; Croft, R. D.; Reid, G.; Schröder, M. *J. Organomet. Chem.* **1989**, *359*, 371. (d) Abel, E. W.; Beer, P. D.; Moss, I.; Orrell, K. G.; Sik, V.; Bates, P. A.; Hursthouse, M. B. *J. Organomet. Chem.* **1988**, *341*, 559. (e) Abel, E. W.; Beer, P. D.; Moss, I.; Orrell, K. G.; Sik, V.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1987**, 978.

(13) (a) Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1180. (b) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Küppers, H.-J.; Schröder, M.; Stötzel, S.; Wieghardt, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1600.

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

(15) Blake, A. J.; Christie, R. M.; Roberts, Y. V.; Sullivan, M. J.; Schröder, M.; Yellowless, L. J. *J. Chem. Soc., Chem. Commun.* **1992**, 848.

(16) $[Cp^*Rh(9S3)]^{2+}$: (a) see ref 23a of this paper. $[Rh(9S3)_2]^{3+}$: (b) Cooper, S. R.; Rawle, S. C.; Yagbasan, R.; Watkin, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 1600. (c) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1861.

(17) (a) Schriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley & Sons, Inc.: New York, 1986. (b) Wayda, A. L., Darensbourg, M. Y., Eds. *Experimental Organometallic Chemistry*; ACS Symposium Series *357*; American Chemical Society: Washington, DC, 1987.

(18) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed.; Pergamon Press: London, 1988.

(19) (a) Blower, P. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 2009. (b) Wolf, R. E., Jr.; Hartman, J. R.; Ochrymowycz, L. A.; Cooper, S. R. *Inorg. Synth.* **1989**, *25*, 122.

(20) Evance, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

(21) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(22) (a) Kim, H.-J.; Jeong, J. H.; Do. Y. *Bull. Kor. Chem. Soc.* **1992**, *13*, 463. (b) Blake, A. J.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1991**, 253. The preparation of the cation 1 has been claimed, but no synthetic, structural, or spectroscopic data were reported. (c) Blake, A. J.; Halcrow, M. A.; Schröder, M. *Acta Crystallogr.* **1993**, *C49*, 85. The X-ray structure of $[Rh(9S3)(CO)(PPh_3)](PF_6)$ was reported.

upon dissolution of the solid was observed. Stirring for 24 h was followed by filtration, and the red filtrate was reduced in volume to *ca.* 3 mL and then treated with an excess amount of Et_2O. The red crude product was collected and recrystallized from $CH_3CN/CH_2Cl_2/Et_2O$, affording analytically pure red crystals in a yield of 65% (99 mg). Anal. Calcd for $C_{34}H_{42}Cl_2O_8S_6Rh_2{\cdot}CH_3CN{\cdot}CH_2Cl_2$: C, 37.86; H, 4.04. Found: C, 37.67; H, 4.15. IR (KBr): 2247, 1573, 1468, 1438, 1408, 1374, 1270, 1176, 1085, 1019, 999, 906, 823, 763, 747, 692, 621, 484, 436 cm^{-1}. ^{1}H-NMR (CD_3CN): δ 1.51 (s, 15 H, Cp*), 1.95 (3 H, CH_3CN), 2.44−2.66 (m, 6 H, 9S3), 3.01−3.21 (m, 6 H, 9S3), 7.41−7.54 (m, 9 H, SPh), 7.91−7.95 (m, 6 H, SPh). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 9.28 (C_5Me_5), 33.91, 39.53 (9S3), 101.15 (d, $^1J_{Rh-C}$ = 7.0 Hz, C_5Me_5), 130.33, 130.93, 131.11, 134.40 (SPh).

[(9S3)Rh(μ-SPh)$_3$IrCp*](ClO_4)$_2$·0.5CH_3CN·0.5CH_2Cl_2 (4(ClO_4)$_2$·0.5CH_3CN·0.5CH_2Cl_2). To 98 mg (0.15 mmol) of solid **3** was added a yellow solution of $[Cp^*Ir(NCMe)_3](ClO_4)_2$ obtained *in situ* from the reaction of $[Cp^*IrCl_2]_2$ (61 mg, 0.08 mmol) with $AgClO_4{\cdot}H_2O$ (68 mg, 0.30 mmol) in 15 mL of CH_3CN for 1.5 h. As the reaction proceeded, the compound **3** gradually dissolved and the solution was changed from yellow to orange-red. After the reaction mixture was stirred for 24 h, the solution was filtered. The resulting orange red filtrate was reduced in volume before treating with Et_2O, yielding an orange-red solid. Recrystallization of this solid from $CH_3CN/CH_2Cl_2/Et_2O$ afforded red crystals in a yield of 52% (93 mg). Anal. Calcd for $C_{34}H_{42}Cl_2O_8S_3RhIr{\cdot}0.5CH_3CN{\cdot}0.5CH_2Cl_2$: C, 35.53; H, 3.74. Found: C, 35.84; H, 3.92. IR (KBr): 2249, 1574, 1469, 1439, 1408, 1377, 1087, 1024, 998, 907, 823, 763, 748, 692, 622, 485, 437 cm^{-1}. ^{1}H-NMR (CD_3CN): δ 1.57 (s, 15 H, Cp*), 1.95 (s, CH_3CN), 2.45−2.58 (m, 6 H, 9S3), 2.93~3.14 (m, 6 H, 9S3), 7.44−7.53 (m, 9 H, SPh), 7.84−7.89 (m, 6 H, SPh). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 9.29 (C_5Me_5), 33.90, 39.61 (9S3), 95.01 (C_5Me_5), 130.37, 130.44, 131.52, 134.01 (SPh).

X-ray Structural Determination. (A) [Rh(9S3)(PPh$_3$)(I)$_2$]ClO$_4$. A dark red single crystal grown by slow vapor diffusion of Et_2O into a solution of the complex in CH_3CN was mounted on a glass fiber, and diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo *K*α radiation at 24 °C. Accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections. Intensity data were collected in the $\omega-2\theta$ scan mode to a maximum 2θ of 48°. Three reflections $(65\bar{3}, \bar{3}2\bar{7}, \bar{1}47)$ were measured every 6000 seconds, and the intensities of three standards remained constant within experimental error throughout data collection. Of the 3850 unique reflections measured, 3432 were considered observed ($F_o > 6\sigma(F_o)$) and used in subsequent structural analysis. Data were corrected for Lorentz and polarization effects. No absorption correction was applied.

The structure was solved by locating rhodium and iodide atoms in an electron density map by use of heavy-atom methods (SHELXS 86).[23] All remaining non-hydrogen atoms were found by iterative cycles of full-matrix least-squares refinement and difference-Fourier synthesis.[24] All non-hydrogen atoms were refined anisotropically. The phenyl rings of PPh_3 ligand were refined as rigid groups with fixed bond lengths (d_{C-C} = 1.395 Å) and angles (120°). All hydrogen atoms were included at calculated positions (d_{C-H} = 1.08 Å) with a fixed *U* value of 0.08 Å^2. All calculations were performed on the IBM RS/6000 workstation. In the final refinement cycles a weighting scheme of the form $w = 2.6684/[\sigma^2(F)]$ was employed. Refinement converged with *R* (R_w) = 0.038 (0.030) and $(\Delta/\sigma)_{max}$ was 0.001. The greatest residual maximum of 1.48 e Å^{-3} was in the vicinity of I1. A structure determination summary is given in Table 1, and positional and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table 2.

(B) [(9S3)Rh(μ-SPh)$_3$IrCp*](ClO_4)$_2$·0.5CH_2Cl_2·0.5CH_3CN. A red plate crystal suitable for X-ray work was grown by slow vapor diffusion of Et_2O into a solution of the complex in CH_3CN/CH_2Cl_2 and mounted on a glass fiber. Diffraction measurements were made on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation at 21 °C. Accurate unit cell parameters and crystal orientation matrix were determined from the least-squares fit of 24 accurately centered reflections in the range 11.52° ≤ θ ≤ 13.89°. Intensity data were collected in the range $0 \le h \le 26$, $0 \le k \le 17$, $-12 \le l \le 12$ with $\omega-2\theta$ scan mode to a maximum 2θ of 46°. The intensities of three standard reflections measured every 6000 seconds as general check on crystal and instrument stability decreased by 2.54% during the course of the data collection. Of the 4669 unique reflections measured, 2591 were considered as observed ($F_o > 6\sigma(F_o)$) and used in subsequent

Table 1. Crystallographic Data[a]

[Rh(9S3)(PPh$_3$)(I)$_2$]ClO$_4$	
$C_{24}H_{27}ClI_2O_4PRhS_3$	fw = 898.8
a = 15.416(3) Å	$P2_1/a$, monoclinic (No. 14)
b = 13.440(1) Å	*T* = 25 °C
c = 13.987(2) Å	λ(Mo Kα) = 0.710 73 Å
β = 91.14(1)°	μ(Mo Kα) = 28.86 cm^{-1}
V = 2987.4 Å^3	ϱ_{calcd} = 2.05 g cm^{-3}
Z = 4	
$R(F_o)$ = 0.038	
$R_w(F_o)$ = 0.030	
[(9S3)Rh(μ-SPh)$_3$IrCp*](ClO_4)$_2$·0.5CH_3CN·0.5CH_2Cl_2	
$C_{35.5}H_{44.5}Cl_3O_8N_{0.5}S_6IrRh$	fw = 1200.1
a = 24.554(5) Å	$P2_1/n$, monoclinic (No. 14)
b = 15.706(2) Å	*T* = 21 °C
c = 11.725(1) Å	λ(Mo Kα) = 0.710 73 Å
β = 98.36(2)°	μ(Mo Kα) = 37.15 cm^{-1}
V = 4473.6 Å^3	ϱ_{calcd} = 1.78 g cm^{-3}
Z = 4	
$R(F_o)$ = 0.067	
$R_w(F_o)$ = 0.059	

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$.

Table 2. Positional and Equivalent Isotropic Thermal Parameters[a] (Å^2) for Non-Hydrogen Atoms of [Rh(9S3)(PPh$_3$)(I)$_2$](ClO$_4$)

atom	*x*	*y*	*z*	U_{eq}[b]
Rh	0.18962(4)	0.08896(4)	0.15407(4)	0.0267
I1	0.06053(4)	0.18624(6)	0.06248(4)	0.0719
I2	0.26388(4)	0.25435(4)	0.22082(4)	0.0601
P1	0.1084(1)	0.0707(1)	0.2963(1)	0.0282
S1	0.3072(1)	0.0022(2)	0.2138(2)	0.0592
S4	0.2697(1)	0.1167(2)	0.0147(1)	0.0411
S7	0.1380(2)	−0.0538(2)	0.0829(2)	0.0703
C2	0.3882(5)	0.0030(8)	0.1181(6)	0.0804
C3	0.3800(5)	0.0927(7)	0.0547(5)	0.0555
C5	0.2491(5)	0.0080(7)	−0.0601(5)	0.0568
C6	0.1594(6)	−0.0340(7)	−0.0435(6)	0.0754
C8	0.2191(8)	−0.1470(7)	0.1149(8)	0.1112
C9	0.2695(7)	−0.1248(7)	0.2033(7)	0.0960
C11	0.0749(3)	0.1822(4)	0.3621(2)	0.0304
C12	0.0481(3)	0.2685(4)	0.3147(2)	0.0431
C13	0.0145(3)	0.3480(4)	0.3663(2)	0.0511
C14	0.0077(3)	0.3412(4)	0.4654(2)	0.0488
C15	0.0345(3)	0.2549(4)	0.5128(2)	0.0512
C16	0.0681(3)	0.1754(4)	0.4612(2)	0.0422
C21	0.0063(3)	0.0023(3)	0.2801(3)	0.0297
C22	0.0078(3)	−0.0959(3)	0.2481(3)	0.0346
C23	−0.0691(3)	−0.1505(3)	0.2417(3)	0.0465
C24	−0.1473(3)	−0.1069(3)	0.2673(3)	0.0484
C25	−0.1488(3)	−0.0086(3)	0.2993(3)	0.0440
C26	−0.0719(3)	0.0460(3)	0.3057(3)	0.0376
C31	0.1692(3)	0.0008(3)	0.3875(4)	0.0323
C32	0.2454(3)	0.0437(3)	0.4239(4)	0.0466
C33	0.2962(3)	−0.0074(3)	0.4914(4)	0.0610
C34	0.2708(3)	−0.1015(3)	0.5224(4)	0.0615
C35	0.1947(3)	−0.1444(3)	0.4860(4)	0.0596
C36	0.1439(3)	−0.0933(3)	0.4185(4)	0.0448
Cl	0.4177(2)	0.1195(2)	0.7541(2)	0.0526
O1	0.4974(3)	0.1082(4)	0.7095(4)	0.0721
O2	0.4328(5)	0.1658(6)	0.8421(5)	0.1272
O3	0.3812(5)	0.0286(5)	0.7669(7)	0.1607
O4	0.3659(4)	0.1860(6)	0.7018(6)	0.1321

[a] Units of each esd in parentheses are those of the least significant digit of the corresponding parameters. [b] The isotropic equivalent thermal parameter is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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(23) Sheldrick, G. M. *SHELXS 86. Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.

(24) Sheldrick, G. M. *SHELX 76. System of Crystallographic Computer Program*; University of Cambridge: Cambridge, England, 1976.

structural analysis. All the intensity data were corrected for Lorentz and polarization effect but not for absorption.

The structure was solved by the heavy-atom method (SHELXS 86).[23] All remaining non-hydrogen atoms were found by iterative cycles of full-matrix least-squares refinement and difference-Fourier synthesis.[24] All but carbon and hydrogen atoms were assigned anisotropic thermal parameters. The phenyl rings of three thiolates were refined as rigid groups with fixed bond lengths (d_{C-C} = 1.395 Å) and angles (120°). The cyclopentadienyl ring of Cp* was refined as a regular pentagon (d_{C-C} = 1.420 Å, angle = 108°), but five methyl groups were freely refined. All hydrogen atoms were included at calculated positions (d_{C-H} = 1.08 Å) with fixed U values of 0.08 Å^2. The ClO_4^- anions were found to be affected by high thermal motion (or disorder). Attempts to solve the disorder in terms of a "partial" atom were unsuccessful. The best fit was found by allowing the atoms to vary anisotropically. As a consequence the U_{ij} temperature factors for these atoms are rather high in values. At an intermediate stage in refinement, several peaks due to highly disordered solvents were found in a ΔF map. Among them, two highest peaks (2.39, 1.86 e Å^{-3}) were assumed to be Cl atoms of the disordered CH_2Cl_2 unit. Another three peaks, in near linear geometry, were assumed to belong to a CH_3CN solvent. Their positional parameters were refined with the site occupancy factors of 0.5. All calculations were performed on the IBM RS/6000 workstation. In the final cycles of refinement, a weighting scheme of $w = 1.5985/[\sigma^2(F) + 0.0008\ (F^2)]$ was used. Refinement converged with R (R_w) = 0.067 (0.059) for 278 variables and $(\Delta/\sigma)_{max}$ was 0.000. On the final ΔF map, several highest peaks (1.86−1.34 e Å^{-3}) were in the vicinities of Ir1 and Rh1. Details of the crystal structure determination are summarized in Table 1, and positional and isotropic thermal parameters of the non-hydrogen atoms are listed in Table 3. Complete lists of anisotropic thermal parameters and hydrogen atom coordinates are given in the supplementary material.

Other Physical Measurements. Infrared spectra were measured as KBr pellets on a Bomem MB-100 FTIR spectrometer operating between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and were referenced to a 1601 cm^{-1} band of polystyrene film. ^{1}H-NMR spectra were recorded either at 200.13 MHz on a Bruker AC 200 or 300.13 MHz on a Bruker AM 300 spectrometer, and $^{13}C\{^1H\}$-NMR spectra, at 50.324 MHz on a Bruker AC200 instrument; spectra were referenced to internal solvent peaks. Proton-decoupled ^{31}P-NMR spectra were obtained at 121.496 MHz on a Bruker AM 300 instrument and referenced relative to external solutions of 85% H_3PO_4 in D_2O with positive chemical shifts referring to lower field strength. Elemental analyses for C, H, and N were performed by Han Yang Chemical Cooperation Research Center, Taejon, Korea.

Results and Discussion

Synthesis and Oxidative Decarbonylation Reactions of $[Rh(9S3)(CO)(PPh_3)]^+$ (1). In our preliminary report,[22a] the preparation scheme and the spectroscopic data for the cation **1** and its Ir analogue have been described along with the synthesis of $[Cp^*M(9S3)]^{2+}$ (M = Co, Rh, Ir) and the structure of $[Cp^*Rh(9S3)]^{2+}$. Although the synthetic procedure of the cation **1** is rather straightforward, it deserves further comment as well as full description due to the apparent conflict between the initial claim[22b] on the preparation of **1** by reacting 9S3 with $RhCl(CO)(PPh_3)_2$ and our observation on the lack of any reactivity between $M(CO)(PPh_3)_2$ (M = Rh, Ir) and 9S3 in CH_3CN. Treatment of $MCl(CO)(PPh_3)_2$ with $AgClO_4$ prior to the addition of 9S3 is required to generate the cations $[M(9S3)(CO)(PPh_3)]^+$ in CH_3CN, indicating the involvement of *in situ* generated $[M(CO)(PPh_3)_2(CH_3CN)]^+$ in reaction with 9S3. The isolation[22a] of $[Ir(9S3)(CO)(PPh_3)]^+$ as a salt of [10-*endo*-$(SnPh_3)$-μ-H-7,8-*nido*-$C_2B_9H_{10}]^-$ from the reaction system of well-characterized [*trans*-$Ir(CO)(PPh_3)_2(CH_3CN)$][10-*endo*-$(SnPh_3)$-μ-H-7,8-*nido*-$C_2B_9H_{10}]$[25] and 9S3 in CH_3CN supports the role of $[M(CO)(PPh_3)_2(CH_3CN)]^+$ formation in generating $[M(9S3)(CO)(PPh_3)]^+$.

Table 3. Positional and Isotropic Thermal Parameters[a] (Å^2) of $[(9S3)Rh(\mu SPh)_3IrCp^*](ClO_4)_2{\cdot}0.5CH_3CN{\cdot}0.5CH_2Cl_2$

atom	*x*	*y*	*z*	U_{eq}/U_{iso}[b]
Ir1	0.19507(4)	0.22195(8)	0.47059(10)	0.040*
Rh1	0.06578(8)	0.23567(15)	0.4978(2)	0.043*
S1	−0.0012(3)	0.1342(5)	0.4378(8)	0.066*
S4	0.0333(3)	0.2462(5)	0.6726(7)	0.065*
S7	0.0060(3)	0.3419(5)	0.4239(8)	0.071*
S11	0.1431(3)	0.3222(5)	0.5663(7)	0.050*
S21	0.1130(3)	0.2307(6)	0.3338(6)	0.051*
S31	0.1343(3)	0.1301(5)	0.5557(7)	0.052*
Cl1	0.1941(4)	0.8532(7)	0.5304(11)	0.076*
Cl2	0.0739(5)	0.7284(11)	0.0525(13)	0.111*
O11	0.182(2)	0.865(3)	0.416(3)	0.249*
O12	0.1747(11)	0.781(2)	0.559(3)	0.179*
O13	0.1661(11)	0.916(2)	0.575(3)	0.188*
O14	0.2455(14)	0.855(3)	0.569(4)	0.284*
O21	0.0213(10)	0.739(2)	0.077(2)	0.170*
O22	0.0966(14)	0.654(2)	0.056(5)	0.267*
O23	0.1050(4)	0.767(3)	0.144(4)	0.261*
O24	0.078(2)	0.757(4)	−0.043(3)	0.310*
C2	−0.0403(12)	0.125(2)	0.557(3)	0.07(1)
C3	−0.0069(14)	0.150(2)	0.673(3)	0.09(1)
C5	−0.0205(12)	0.324(2)	0.649(3)	0.07(1)
C6	−0.0101(12)	0.386(2)	0.554(3)	0.07(1)
C8	−0.0573(12)	0.282(2)	0.368(2)	0.09(1)
C9	−0.0483(12)	0.191(2)	0.326(3)	0.07(1)
C11	0.1424(6)	0.4248(11)	0.5006(15)	0.044(8)
C12	0.1266(6)	0.4428(11)	0.3840(15)	0.050(8)
C13	0.1324(6)	0.5251(11)	0.3427(15)	0.061(9)
C14	0.1539(6)	0.5895(11)	0.4181(15)	0.056(9)
C15	0.1697(6)	0.5715(11)	0.5347(15)	0.07(1)
C16	0.1639(6)	0.4891(11)	0.5760(15)	0.07(1)
C21	0.0977(7)	0.1361(10)	0.257(2)	0.044(8)
C22	0.0625(7)	0.1442(10)	0.153(2)	0.07(1)
C23	0.0494(7)	0.0729(10)	0.084(2)	0.07(1)
C24	0.0716(7)	−0.0063(10)	0.118(2)	0.063(9)
C25	0.1069(7)	−0.0144(10)	0.222(2)	0.07(1)
C26	0.1199(7)	0.0568(10)	0.292(2)	0.058(9)
C31	0.1491(7)	0.1180(11)	0.704(2)	0.056(9)
C32	0.1273(7)	0.0467(11)	0.752(2)	0.066(9)
C33	0.1364(7)	0.0342(11)	0.871(2)	0.07(1)
C34	0.1674(7)	0.0930(11)	0.942(2)	0.07(1)
C35	0.1893(7)	0.1644(11)	0.894(2)	0.09(1)
C36	0.1801(7)	0.1769(11)	0.775(2)	0.07(1)
C41	0.2529(7)	0.220(2)	0.3491(12)	0.041(7)
C42	0.2643(7)	0.293(2)	0.4207(12)	0.060(9)
C43	0.2794(7)	0.264(2)	0.5358(12)	0.08(1)
C44	0.2773(7)	0.174(2)	0.5354(12)	0.10(1)
C45	0.2610(7)	0.147(2)	0.4200(12)	0.07(1)
C46	0.2408(11)	0.218(2)	0.226(2)	0.077(9)
C47	0.2648(14)	0.383(2)	0.373(3)	0.09(1)
C48	0.2945(14)	0.328(2)	0.635(3)	0.10(1)
C49	0.291(2)	0.120(3)	0.636(3)	0.13(2)
C50	0.2646(13)	0.056(2)	0.384(3)	0.09(1)
C(S)	0.118(2)	0.350(4)	0.922(5)	0.05(2)
Cl(S1)	0.0918(13)	0.439(2)	0.857(3)	0.21(1)
Cl(S2)	0.1205(14)	0.371(2)	0.050(3)	0.24(2)
N(S1)	0.069(2)	0.489(4)	0.771(5)	0.09(2)
C(S2)	0.031(4)	0.520(6)	0.826(8)	0.14(3)
C(S3)	−0.009(5)	0.541(8)	0.924(10)	0.26(6)

[a] See footnote *a* in Table 2. [b] Values with an asterisk denote atoms refined anisotropically and are given in the form of equivalent isotropic displacement parameters defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The Rh(I) crown thioether complex $\mathbf{1ClO_4}$ undergoes oxidative decarbonylation reactions to give new Rh(III) complexes of 9S3. Attempts at making thiolato and sulfido Rh(III) complexes of 9S3 were performed by reacting $\mathbf{1ClO_4}$ with benzene disulfide and elemental sulfur, respectively, affording CO group free red solid products[26] in both cases. Reaction of $\mathbf{1ClO_4}$ with I_2 gave a new oxidative decarbonylation reaction product $[Rh(9S3)(PPh_3)(I)_2]^+$ (**2**) as a perchlorate salt in good yield.

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(25) Kim, J.; Kim, S.; Do. Y. *J. Chem. Soc., Chem. Commun.* **1992**, 938.

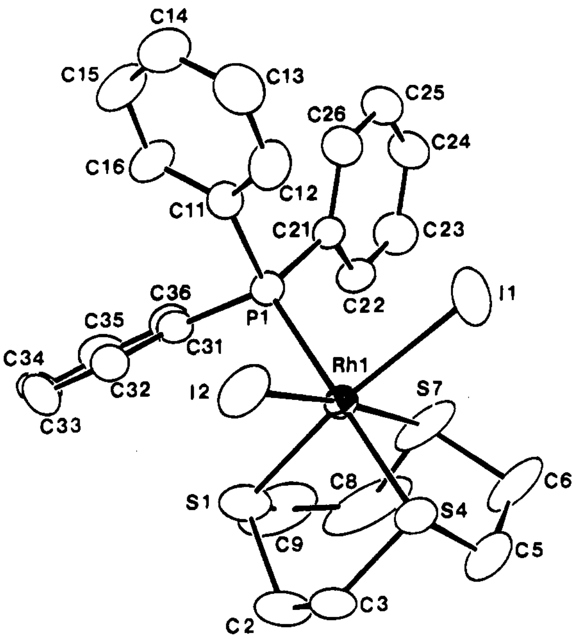

Figure 1. Molecular structure of $[Rh(9S3)(PPh_3)(I)_2]^+$ (**2**), showing the atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

Structure of $[Rh(9S3)(PPh_3)(I)_2](ClO_4)$ ($2ClO_4$). The crystal structure $2ClO_4$ consists of discrete cation **2** and ClO_4^- anion. The structure of the ClO_4^- anion is not unusual and will not be discussed further. The structure of mononuclear Rh(III) complex cation **2**, displayed in Figure 1, shows no overall symmetry and is isostructural with isoelectronic $Ru(9S3)(PPh_3)(Cl)_2$.[27] Two iodide groups in **2** are disposed in cis geometry around the octahedral Rh center.

Selected interatomic distances and angles for $2ClO_4$ are listed in Table 4. The Rh(III)−S distances in **2** fall into two cartegories of long (Rh1−S4 = 2.358(2) Å) and short (2.297(2) and 2.298(2) Å) values which can be compared to the average Rh−S values in $[Cp^*Rh(9S3)](ClO_4)_2{\cdot}CH_3CN$ (2.340 Å),[12d] $[Rh(9S3)_2](CF_3SO_3)_3$ (2.341 Å),[16b] and $[Rh(9S3)_2](PF_6)_2$ (2.333 Å).[16e] The large variance of Rh−S distance in **2** can be ascribed to the different extent of trans influence of iodides and triphenylphosphine. A similar metal−sulfur bond variance owing to trans influence has been observed in a series of Os−9S3 complexes.[9a] The lengthening of the Rh−P bond (2.383(1) Å) in **2** compared to the range (2.248−2.295 Å) observed in a set of $[Cp^*Rh(PPh_3)X_2]$ (X = Cl, Br)[28] can be considered as a manifestation of trans influence of 9S3 on the phosphine. Consistent with this observation is that the coupling constant $^1J_{Rh-P}$ = 96 Hz for $2ClO_4$ is smaller than those ($^1J_{Rh-P}$ = 137−147 Hz) for $[Cp^*Rh(PPh_3)(X)_2]$.[28] The average Rh−I distance of 2.676 Å is in intemediate range between those of $[(TPB)Rh(CO)(I)_2]$ (2.642 Å)[29] and $[Cp^*Rh(I)_2]_2$ (2.724 Å).[30]

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[Rh(9S3)(PPh_3)(I)_2](ClO_4)$

Rh1−I1	2.685(1)	Rh1−I2	2.661(1)
Rh1−P1	2.385(2)	Rh1−S1	2.298(2)
Rh1−S4	2.358(2)	Rh1−S7	2.297(2)
S1−C2	1.848(8)	C2−C3	1.500(11)
C3−S4	1.809(7)	S4−C5	1.821(8)
C5−C6	1.516(10)	C6−S7	1.825(8)
S7−C8	1.818(12)	C8−S9	1.478(14)
S1−C9	1.808(11)		
I1−Rh1−I2	94.0(<1)	P1−Rh1−I1	93.0(<1)
P1−Rh1−I2	91.3(<1)	S1−Rh1−I1	172.8(1)
S4−Rh1−I1	85.6(1)	S7−Rh1−I1	87.3(1)
S1−Rh1−I2	88.0(1)	S4−Rh1−I2	85.9(1)
S7−Rh1−I2	173.2(1)	S1−Rh1−P1	93.9(1)
S4−Rh1−P1	176.8(1)	S7−Rh1−P1	95.3(1)
S1−Rh1−S4	87.6(1)	S1−Rh1−S7	89.9(1)
S4−Rh1−S7	87.5(1)	C9−S1−C2	99.6(5)
S1−C2−C3	112.5(6)	C2−C3−S4	113.1(6)
C3−S4−C5	100.8(4)	S4−C5−C6	111.1(5)
C5−C6−S7	112.7(6)	C6−S7−C8	101.7(5)
S7−C8−C9	114.5(7)	C8−C9−S1	114.9(7)

Reaction Product of $2ClO_4$ with Benzenethiol and Synthesis of Dinuclear Rh(III) Complexes of 9S3. The existence of a trans influence in **2** suggests that the ligands *trans* to 9S3 might be susceptible to substitution reactions. In fact, the compound $2ClO_4$ reacts with excess amounts of PhSH in CH_3CN in the presence of NEt_3 to give insoluble red neutral species with the empirical formula of $Rh(9S3)(SPh)_3{\cdot}CH_3CN$ (**3**). Full direct characterization of **3** was hampered by its insoluble nature in most organic solvents, but its tendency to form dinuclear complexes via tris-μ-SPh bridges lends not only a novel route to heterodinuclear system but also a solution to confirm the entity of **3** otherwise established only by elemental analysis and IR spectroscopic data. The ability of thiolate groups in **3** to bridge an additional metal unit has been tested as summarized in Scheme 1, providing a systematic route to unprecedented novel dinuclear cationic species of $[(9S3)Rh(\mu\text{-}SPh)_3MCp^*]^{2+}$ (M = Rh; Ir, **4**). Spectroscopic data for these species are similar and reveal the common presence of ligated 9S3, Cp*, and benzenethiolate ligands in the ratio of 1:1:3, respectively, indicating that both cations have the same structural core whose nature for M = Ir was determined by single crystal X-ray analysis.

Structure of $[(9S3)Rh(\mu\text{-}SPh)_3IrCp^*](ClO_4)_2{\cdot}0.5CH_3CN{\cdot}0.5CH_2Cl_2$. Selected interatomic distances and angles for the title complex $4(ClO_4)_2{\cdot}0.5CH_3CN{\cdot}0.5CH_2Cl_2$ are given in Table 5. In the cation **4** whose molecular structure is shown in Figure 2, a $(Cp^*Ir)^{2+}$ moiety interacts with $Rh(9S3)(SPh)_3$ unit, a unit suggested in **3**, via three doubly-bridged benzenethiolate groups, forming a heterodinuclear species with Ir••Rh interatomic distance of 3.244(2) Å. Three benzenethiolates and 9S3 unit are disposed such that the Ir−Rh vector in the $Ir(\mu\text{-}SPh)_3Rh(9S3)$ fragment approaches a 3-fold axis. Two planes defined by three 9S3 sulfur atoms and three thiolate sulfur atoms are nearly parallel with a dihedral angle of 1.6°. Three bond distances from Rh to 9S3 sulfur atoms vary, but such a large variance observed in **2** is not present in **4**. The observed Rh−9S3 sulfur distances in **2** and **4** add to the list of examples[16,31]

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(26) Both products are lacking in crystallinity, hampering complete structural characterizations. Spectroscopic data suggest the following formulas for the products. $[Rh(9S3)(PPh_3)(SPh)]_2(ClO_4)_4$: Anal. Calcd for $C_{60}H_{64}Cl_4O_{16}P_2S_8Rh_2$: C, 42.2; H, 3.78. Found: C, 42.7; H, 4.15. IR (KBr), 1570, 1480, 1463, 1434, 1403, 1274, 1084, 1022, 998, 905, 820, 746, 694, 622, 525, 510, 494 cm^{-1}. ^1H-NMR (CD_3CN): δ 2.44 (m), 2.83 (m), 3.09 (m) (1:1:1, 9S3), 7.07−7.89 (m, PPh_3 + SPh). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 36.70, 36.91 (d, $^3J_{PC}$ = 7.0 Hz), 37.14 (9S3), 127.29, 128.41, 135.30, 136.37 (SPh), 128.50 (d, J = 9.2 Hz), 131.73 (d, J = 2.7 Hz), 134.78 (d, J = 8.3 Hz) (PPh_3). $^{31}P\{^1H\}$-NMR ($CH_2Cl_2/CDCl_3$): δ 17.76 (d, $^1J_{Rh-P}$ = 113 Hz). $[Rh(9S3)(PPh_3)(S_6)](ClO_4){\cdot}CH_3CN$: Anal. Calcd for $C_{24}H_{27}ClO_4PS_9Rh{\cdot}CH_3CN$: C, 35.6; H, 3.44; N, 1.59. Found: C, 35.4; H, 3.83; N, 1.26; IR (KBr): 1480, 1433, 1402, 1274, 1083, 997, 935, 905, 821, 747, 693, 621, 524, 513, 488, 456 cm^{-1}. ^1H-NMR (CD_3CN): δ 2.24−2.33 (m), 2.81−2.97 (m), 3.11−3.20 (m), 3.22−3.36 (m), 3.46−3.58 (m) (3:2:2:3:2, 9S3), 7.46−7.82 (m, PPh_3). $^{31}P\{^1H\}$-NMR (CD_3CN/CH_3CN): δ 17.43 (d, $^1J_{Rh-P}$ = 108 Hz).

(27) Hill, A. F.; Alcock, N. W.; Cannadine, J. C.; Clark, G. R. *J. Organomet. Chem.* **1992**, *426*, C40 and ref 8b of this paper.

(28) Jones, W. D.; Kuybendall, V. L. *Inorg. Chem.* **1991**, *30*, 2615.

(29) Cocivera, M.; Desmond, T. J; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O'Sullivan, D. J. *Organometallics* **1982**, *1*, 1125. TPB = tris(pyrazolyl)borate.

(30) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1979**, *18*, 2918.

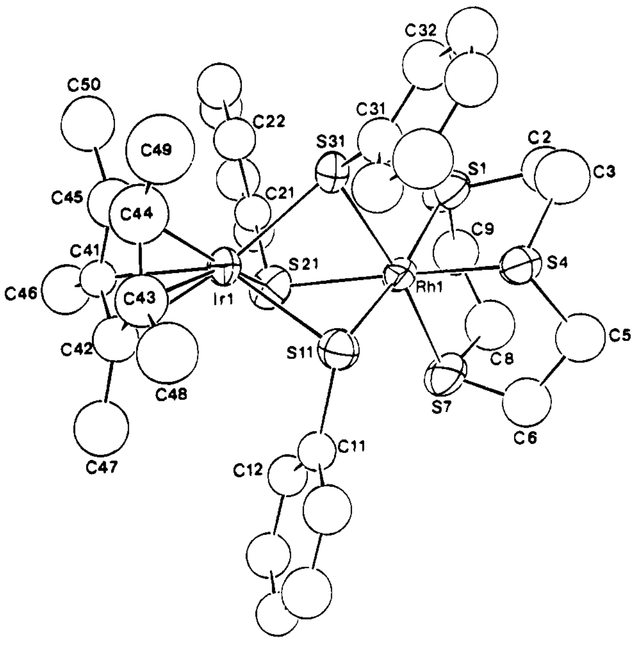

Figure 2. Perspective drawing of $[(9S3)Rh(\mu\text{-}SPh)_3IrCp^*]^{2+}$ (**4**), showing the atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

of a Rh(III)$-SR_2$ (R = sp^3-C) bonding interaction. The relative extent of trigonal flattening of 9S3 in **4** is the largest among Rh(III)$-$9S3 complexes as measured by average chelating S$-$Rh$-$S angles: 89.9° for **4**, 88.8° for $[Rh(9S3)_2](PF_6)_3$,[16c] 88.6° for $[Rh(9S3)_2](CF_3SO_3)_3$,[16b] and 88.3° for **2** and $[Cp^*Rh(9S3)]^{2+}$.[16a]

Examples of dinuclear complexes supported by 9S3 are very limited and include $[TlCl_2Ru(PPh_3)(9S3)]_2^{2+}$ containing a $RuCl_2Tl_2Cl_2Ru$ ladder core,[15] $[RuCl(PPh_3)(9S3)]_2^{2+}$ with a planar Ru_2Cl_2 rhomb,[15] and $[Ni_2Cl_3(9S3)]^{2+}$ consisting of two face-shared octahedra.[32] These multinuclear complexes are symmetric with respect to the bridging unit in them since two halves of each cation are related by an inversion center for the ruthenium species or by a plane of three bridging chlorides for the nickel compound. On the other hand, the dinuclear Rh(III) complexes derived from **3** constitute a different class of multinuclear 9S3 complexes with nonsymmetric feature with respect to the bridging unit.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) of $[(9S3)Rh(\mu\text{-}SPh)_3IrCp^*](ClO_4)_2{\cdot}0.5CH_3CN{\cdot}0.5CH_2Cl_2$

Ir1•••Rh1	3.244(2)	Ir1−S11	2.405(7)
Ir1−S21	2.389(6)	Ir1−S31	2.395(8)
Rh1−S11	2.378(8)	Rh1−S21	2.387(7)
Rh1−S31	2.390(8)	Rh1−S1	2.325(9)
Rh1−S4	2.310(8)	Rh1−S7	2.306(9)
Ir1−C41	2.15(2)	Ir1−C42	2.18(2)
Ir1−C43	2.20(2)	Ir1−C44	2.19(2)
Ir1−C45	2.16(2)		
Rh1−S11−Ir1	85.4(3)	Rh1−S21−Ir1	85.5(2)
Rh1−S31−Ir1	85.3(3)	S11−Ir1−S21	79.8(3)
S21−Ir1−S31	78.2(2)	S21−Ir1−S31	78.4(3)
S11−Rh1−S21	80.4(3)	S11−Rh1−S31	78.8(2)
S21−Rh1−S31	78.5(3)	S11−Rh1−S1	171.6(3)
S11−Rh1−S4	91.2(3)	S11−Rh1−S7	98.4(3)
S21−Rh1−S1	98.0(3)	S21−Rh1−S4	171.0(3)
S21−Rh1−S7	94.5(3)	S31−Rh1−S1	92.8(3)
S31−Rh1−S4	96.7(3)	S31−Rh1−S7	172.8(3)
S1−Rh1−S4	89.8(3)	S1−Rh1−S7	89.9(3)
S4−Rh1−S7	90.0(3)		

Conclusions

A novel route to dinuclear 9S3 complex cations of the type $[(9S3)Rh(\mu\text{-}SPh)_3MCp^*]^{2+}$ (M = Rh, Ir) has been devised. The mononuclear Rh(I) complex $[Rh(9S3)(PPh_3)(CO)]^+$ is reactive toward oxidative decarbonylation reactions, and with I_2, a new oxidative addition product $[Rh(9S3)(PPh_3)(I)_2]^+$ results. X-ray structural analysis shows that $[Rh(9S3)(PPh_3)(I)_2]^+$ derives its substitution reactivity from the trans influence. In the presence of excess benzenethiol and NEt_3, it gives an insoluble red neutral solid with the empirical formula of $Rh(9S3)(SPh)_3{\cdot}CH_3CN$ whose proven ability in forming a new class of dinuclear 9S3 complexes should provide extended access to new multinuclear 9S3 complexes.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen positions, and complete bond distances and angles for $2ClO_4$ and $4(ClO_4)_2{\cdot}0.5CH_3CN{\cdot}0.5CH_2Cl_2$ (7 pages). Ordering information is given on any current masthead page.

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(31) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(32) Blake, A. J.; Halcrow, M. A.; Schröder, M. *Acta Crystallogr.* **1992**, *C48*, 1844.