(aromatic protons); IR Nujol 1672, 1630 cm^{-1}. Anal. Calcd for $C_{33}H_{46}N_2Cl_2$: C, 73.18; H, 8.56; N, 5.17. Found: C, 73.20; H, 8.97; N, 5.44.

2e (91%): IR (KBr) 2196 cm^{-1} ($C\equiv N$). Anal. Calcd for $C_{64}H_{92}N_4Cl_2Co$: C, 73.40; H, 8.86; N, 5.35. Found: C, 73.11; H, 9.00; N, 5.55.

Reaction of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ with Benzyl Bromide. To a solution of **1a** (0.48 g, 0.4 mmol) and 2,6-xylyl isocyanide (0.54 g, 4.12 mmol) in benzene (10 mL) was added benzyl bromide (0.33 g, 1.93 mmol) in benzene (5 mL) at room temperature. After 1 h, the green solid (0.58 g, 95.2%) of **2d** was filtered. The yellow filtrate was chromatographed on alumina. Eluting with hexane gave a pale yellow solution, from which 2,6-xylyl isocyanide was recovered. The second elution with benzene gave a yellow solution. The removal of the solvent and crystallization of the residue from hexane gave yellow crystals (0.36 g, 62.2%) of **4**: mp 153 °C; mass spectrum, *m/e* (mol wt 706.9); IR (KBr) 1670, 1630 cm^{-1} ($C=N$); ^1H NMR ($CDCl_3$) δ 1.67 (b s, Me), 1.97 (b s, Me), 3.72 (b s, CH_2), 6.5–7.6 (aromatic protons); ^{13}C NMR ($CDCl_3$) δ 18.15, 18.58 (CH_3), 40.80 (CH_2), 125.23, 125.65 (outer and inner orthocarbons in aromatic carbons), 134.17 (CH_2C), 123.30, 123.61, 126.61, 127.58, 127.82, 128.17, 129.70 (other aromatic carbons), 147.19 (outer and inner NC, accidental degeneracy), 164.86, 165.09 (outer and inner imino *C*).

Registry No. 1a, 57116-94-6; **1b**, 57116-97-9; **1c**, 116785-56-9; **1d**, 57116-95-7; **1e**, 116785-57-0; **2a**, 67662-53-7; **2b**, 116840-41-6; **2d**, 64707-32-0; **2e**, 116840-42-7; **4**, 64694-36-6; CCl_4, 56-23-5; CBr_4, 558-13-4; $CO_2(2,4,6\text{-}Me_3C_6H_2NC)_8$, 67662-51-5; $CO_2(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_8$, 67662-52-6; $CO_2(2,6\text{-}Me_2C_6H_3NC)_8$, 64707-28-4; $2,4,6\text{-}Me_3C_6H_2NC$, 57116-96-8; $2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC$, 24139-49-9; dicobalt octakis(2,4-di-*tert*-butyl-6-methylphenyl isocyanide), 116862-77-2; 2,6-xylyl isocyanide, 2769-71-3; 2,4-di-*tert*-butyl-6-methylphenyl isocyanide, 98264-36-9; benzyl bromide, 100-39-0.

Communications

Conformationally Rigid η^3-Cyclopropenyl Complexes of Ruthenium(IV). Crystal and Molecular Structure of $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3Ph_3)Br_2]$

Russell P. Hughes,*[1a] **Jennifer Robbins,**[1a]
David J. Robinson,[1a] **and Arnold L. Rheingold**[1b]

Departments of Chemistry, Dartmouth College
Hanover, New Hampshire 03755, and
University of Delaware, Newark, Delaware 19716

Received June 24, 1988

Summary: Oxidative addition reactions of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}COD)X]$ (COD = 1,5-cyclooctadiene, X = Cl, Br) or tetrameric $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$ with triphenylcyclopropenyl halide salts affords high yields of the novel (η^3-cyclopropenyl)ruthenium(IV) complexes $[Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3Ph_3)X_2]$ (**5**, R = H, X = Cl; **6**, R = H, X = Br; **9**, R = Me, X = Cl). Metathetical replacement of chloride in **5** using bromide or iodide affords the dibromo and diiodo complexes **6** and **7**, respectively. Reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}COD)Cl]$ with triphenylcyclopropenyl bromide affords the mixed chloro–bromo complex $[Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3Ph_3)ClBr]$ (**8**) as well as the dichloro and dibromo complexes **5** and **6**, respectively. The X-ray crystal structure of the bromo derivative **6** confirms the (η^3-cyclopropenyl)metal bonding mode in the solid state: orthorhombic, *Pbca*, a = 20.759 (7) Å, b = 15.656 (5) Å, c = 15.584 (3) Å, V = 5066 (2) Å^3, Z = 8, D_{calcd} = 1.78 g cm^{-3}. In contrast to their fluxional isoelectronic analogue $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3Ph_3)(CO)_2]$ (**2**), $^{13}C\{^1H\}$ and ^1H NMR studies of **5**–**9** establish the conformational rigidity of the cyclopropenyl ligand in solution. Estimates of maximum ($\leq$32 kJ mol^{-1} for **2**) and minimum ($\geq$62 kJ mol^{-1} for **8**) values of $\Delta G^{\ddagger}$ for cyclopropenyl rotation are made from ^{13}C NMR data.

The metallacyclobutadiene/η^3-cyclopropenyl valence isomeric relationship and its possible importance in alkyne metathesis continue to stimulate considerable interest.[2] The synthesis and crystallographic characterization of a number of transition-metal η^3-cyclopropenyl complexes[3,4] have led to the suggestion[4b] that certain structural features pertaining to the metal–C_3 interaction might be correlated with the presence or absence of NMR time scale fluxionality in solution. This is illustrated by the related complexes **1**[4b] and **2**-**4**.[3a] In the formally d^2 W(IV) complex **1** the cyclopropenyl ring is conformationally rigid on the NMR time scale in solution at ambient temperature, and the solid-state structure shows a shorter distance from the metal to the C_3 ring centroid (1.991 Å) than to the C_5 ring centroid (2.046 Å).[4b] Contrasting behavior is exhibited by the formally d^4 M(II) complexes **2**–**4**, in which the cyclopropenyl rings rotate rapidly on the NMR time scale at −80 °C and the solid-state structures of **2** and **3** exhibit shorter distances to the C_5 centroid (**2**, 1.997 Å; **3**, 1.999 Å) than to the C_3 centroid (**2**, 2.055 Å; **3**, 2.067 Å).[3a] Unfortunately, while compounds **1** and **2**–**4** were the closest analogues available for structural and spectroscopic comparison, it was not clear whether the difference in formal d-electron configuration between the metals, steric effects due to different coordination numbers at the metal or different ring substituents, and/or the apparently tighter binding of the C_3 ring in complex **1** were responsible for the difference in rotational barriers between **1** and **2**–**4**. Here we report the synthesis and characterization of conformationally rigid, isostructural, and isoelectronic analogues of complexes **2**–**4**, which provide compelling evidence that none of the above factors correlates directly

---

(1) (a) Dartmouth College. (b) University of Delaware.

(2) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342 and references therein.

(3) (a) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1754 and references therein. (b) Hughes, R. P.; Kläui, W.; Reisch, J. W.; Muller, A. *Ibid.* **1985**, *4*, 1761. (c) Hughes, R. P.; Lambert, J. M. J.; Rheingold, A. L. *Ibid.* **1985**, *4*, 2055. (d) Hughes, R. P.; Lambert, J. M. J.; Whitman, D. W.; Hubbard, J. L.; Henry, W. P.; Rheingold, A. L. *Ibid.* **1986**, *5*, 789. (e) Hughes, R. P.; Lambert, J. M. J.; Hubbard, J. L. *Ibid.* **1986**, *5*, 797. (f) Hughes, R. P.; Lambert, J. M. J.; Reisch, J. W.; Smith, W. L. *Ibid.* **1982**, *1*, 1403.

(4) (a) Schrock, R. R.; Pederson, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574. (b) Churchill, M. R.; Fettinger, J. C.; McCullough, L.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3356. (c) Churchill, M. R.; Ziller, J. W.; Pederson, S. F.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1984**, 485.

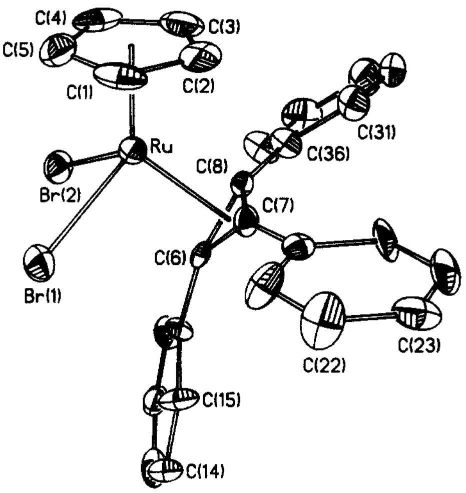


Figure 1. Molecular structure and labeling scheme for 6 with 40% thermal ellipsoids. A molecule of CH_2Cl_2 incorporated in the lattice is not shown. Selected distances (Å): Ru-CNT[C(1)-C(5)], 1.833 (8); Ru-CNT[C(6)-C(8)], 2.036 (8); Ru-Br(1), 2.561 (2); Ru-Br(2), 2.559 (2); Ru-C(6), 2.232 (11); Ru-C(7), 2.184 (12); Ru-C(8), 2.175(11); C(6)-C(7), 1.442 (15); C(7)-C(8), 1.437 (16); C(6)-C(8), 1.404 (16). Selected angles (deg): CNT[C(1)-C(5)]-Ru-CNT[C(6)-C(8)], 128.5 (3); CNT[C(1)-C(5)]-Ru-Br(1), 117.1 (3); CNT[C(1)-C(5)]-Ru-Br(2), 116.6 (3); CNT[C(6)-C(8)]-Ru-Br(1), 99.4 (3); CNT[C(6)-C(8)]-Ru-Br(2), 97.7 (3); Br(1)-Ru-Br(2), 89.2 (1). The phenyl rings are bent back from the cyclopropenyl ring by 21.2° [C(11)-C(16)], 22.2° [C(21)-C(26)], and 20.7° [C(31)-C(36)] (bend-back angles as defined in ref 3a).

with rotational barriers for the cyclopropenyl ring.

Oxidative addition reactions of allylic halides to the ruthenium(II) fragment [Ru(η^5-C_5H_5)X], obtained by displacement of COD from [Ru(η^5-C_5H_5)(η^4-COD)X] (COD = 1,5-cyclooctadiene, X = Cl, Br),[5] are known to give η^3-allylic complexes of Ru(IV).[6a,b] Pentamethylcyclopentadienyl analogues have also been prepared by another route.[6c,d] Analogous oxidative addition reactions with the respective triphenylcyclopropenyl halide salts proceed at room temperature in methanol solution to give good yields of the red-orange, air-stable, crystalline complexes **5** and **6**.[7] The halide ligands are substitutionally labile; metathetical reactions of a methanol solution of **5** with sodium bromide or potasium iodide yield **6** and **7**,[7] while treatment of [Ru(η^5-C_5H_5)(η^4-COD)Cl] with triphenylcyclopropenyl bromide affords a mixture of **5**, **6**, and the mixed halide complex **8**. While **8** was not isolated from the mixture, its characteristic ^1H and $^{13}C\{^1H\}$ NMR resonances[7] were observed after subtraction of the peaks due to pure **5** and **6**. Finally, reaction of the recently reported tetramer [{Ru(η^5-C_5Me_5)Cl}$_4$][8] with triphenylcyclopropenyl chloride in THF provides a facile route to the pentamethylcyclopentadienyl complex **9**.

Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for (CH_2Cl_2 Solvate)

	x	*y*	*z*	*U*[a]
Ru	1952 (1)	9643 (1)	1900 (1)	28 (1)
Br(1)	880 (1)	8843 (1)	2017 (1)	45 (1)
Br(2)	2547 (1)	8220 (1)	2058 (1)	40 (1)
Cl(1)	698 (2)	4463 (3)	968 (4)	124 (3)
Cl(2)	630 (3)	2633 (3)	1103 (4)	117 (3)
C(1)	1533 (7)	10371 (9)	890 (9)	54 (6)
C(2)	1995 (9)	10899 (8)	1286 (9)	67 (7)
C(3)	2607 (8)	10496 (10)	1177 (9)	56 (7)
C(4)	2498 (9)	9773 (9)	686 (9)	50 (6)
C(5)	1858 (8)	9688 (9)	514 (9)	52 (6)
C(6)	1938 (6)	9578 (7)	3330 (7)	27 (4)
C(7)	1764 (5)	10420 (7)	3037 (8)	28 (4)
C(8)	2422 (6)	10136 (6)	3045 (7)	26 (4)
C(9)	654 (7)	3577 (9)	1651 (11)	70 (7)
C(11)	2198 (3)	8383 (5)	4285 (5)	36 (5)
C(12)	2028	7830	4949	45 (5)
C(13)	1404	7847	5283	53 (6)
C(14)	952	8418	4954	49 (6)
C(15)	1122	8971	4290	41 (5)
C(16)	1745	8954	3956	27 (4)
C(21)	664 (4)	11027 (5)	3020 (5)	47 (5)
C(22)	236	11668	3272	63 (7)
C(23)	461	12375	3726	51 (6)
C(24)	1113	12442	3930	67 (7)
C(25)	1541	11802	3679	50 (6)
C(26)	1316	11095	3224	29 (4)
C(31)	3259 (4)	11256 (4)	3176 (6)	41 (5)
C(32)	3888	11504	3367	52 (6)
C(33)	4347	10891	3585	61 (7)
C(34)	4177	10029	3611	54 (6)
C(35)	3548	9781	3419	43 (5)
C(36)	3089	10394	3202	34 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Complexes **5**–**9** are formally d^4 Ru(IV) compounds and as such are isoelectronic with the previously reported Mo(II) and W(II) compounds **2**–**4**.[3a] In order to confirm the overall structural features of these new Ru(IV) compounds and to provide a detailed structural comparison with its closest analogue, the Mo(II) complex **2**, complex **6** was subjected to a single-crystal X-ray diffraction study.[9] The molecular structure of the CH_2Cl_2 solvate of **6** is shown in Figure 1, together with selected distances and angles,

---

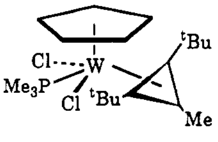
(5) (a) Albers, M. O.; Oosthuizen, H. E.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Organomet. Chem.* **1985**, *282*, C49. (b) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199.

(6) (a) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1986**, 645. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347. (c) Nagashima, H.; Mukai, K.; Itoh, K. *Organometallics* **1984**, *3*, 1314. (d) Nagashima, H.; Mukai, K.; Shiota, Y.; Ara, K.; Itoh, K.; Suzuki, H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1985**, *4*, 1314.

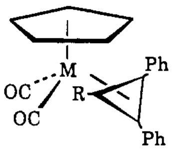
(7) **5**: 66%; mp 210–212 °C dec; ^1H NMR ($CDCl_3$) δ 7.99 (4 H, br m, Ph), 7.81 (2 H, br m, Ph), 7.43 (6 H, br m, Ph), 7.32 (3 H, br m, Ph), 4.99 (5 H, s, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.8, 131.7, 130.0, 129.9, 129.5, 127.4 (Ph), 93.9 (C_5H_5), 93.1 (*C* Ph), 52.8 (2*C* Ph). Anal. Calcd for $C_{26}H_{20}Cl_2Ru$: C, 61.91; H, 4.00; Cl, 14.06. Found: C, 61.75; H, 3.81; Cl, 14.48. **6**: 85%; mp 165 °C dec; ^1H NMR ($CDCl_3$) δ 8.08 (4 H, br m, Ph), 7.92 (2 H, br m, Ph), 7.51 (6 H, br m, Ph), 7.40 (3 H, br m, Ph), 5.17 (5 H, s, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.7, 131.7, 130.2, 130.0, 129.5, 129.3, 127.2, 124.6 (Ph), 93.3 (C_5H_5), 89.2 (*C* Ph), 50.3 (2*C* Ph). Anal. Calcd for $C_{26}H_{20}Br_2Ru$: C, 52.63; H, 3.40; Br, 26.93. Found: C, 52.42; H, 3.19; Br, 26.77. **7**: 88%; mp 160 °C dec; ^1H NMR ($CDCl_3$) δ 8.02 (4 H, br m, Ph), 7.94 (2 H, br m, Ph), 7.48 (6 H, br m, Ph), 7.38 (3 H, br m, Ph), 5.30 (5 H, s, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.1, 131.6, 130.2, 129.8, 129.3, 129.1, 126.9, 125.6 (Ph), 91.8 (C_5H_5), 80.2 (*C* Ph), 46.0 (2*C* Ph). Anal. Calcd for $C_{26}H_{20}I_2Ru$; C, 45.43; H, 2.94; I, 36.93. Found: C, 44.81; H, 2.97; I, 37.02. **8**: ^1H NMR ($CDCl_3$) δ 8.12 (4 H, br m, Ph), 7.90 (2 H, br m, Ph), 7.48 (6 H, br m, Ph), 5.14 (5 H, s, C_5H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.7, 134.6 130.5, 130.1, 129.5, 129.4, 127.4, 127.3, 124.3, 124.0 (Ph), 93.6 (C_5H_5), 91.2 (*C* Ph), 51.8 (*C* Ph), 51.4 (*C* Ph). **9**: 75%; ^1H NMR ($CDCl_3$) δ 8.10 (4 H, br m, Ph), 7.86 (2 H, br m, Ph), 7.41 (6 H, br m, Ph), 7.26 (3 H, br m, Ph), 1.34 (15 H, s, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.1, 131.1, 130.4, 129.1, 128.8, 128.5, 126.9, 126.8 (Ph), 102.3 (*C* Me), 90.0 (*C* Ph), 50.2 (2*C* Ph), 9.1 (Me).

(8) (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.*, submitted for publication. (b) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (c) Koelle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549.

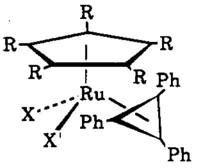
(9) **6**: orthorhombic, *Pbca*, a = 20.759 (7) Å, b = 15.656 (5) Å, c = 15.584 (3) Å, V = 5066 (2) $Å^3$, Z = 8, D_{calcd} = 1.78 g cm^{-3}. A Nicolet R3m/μ diffractometer was used to collect 3655 data (Mo Kα, 4° $\le 2\theta \le$ 46°) of which 3262 were independent and 1715 with $F_o \ge 5\sigma(F_o)$ were used in the collection and refinement. An empirical absorption correction was applied to the data where the crystal was treated as a flat plate. Reflections with a glancing angle <3° to the major face (001) were omitted (μ = 41.7 cm^{-1}). The structure was solved by heavy-atom methods (SOLV). A molecule of CH_2Cl_2 cocrystallizes with the complex. All remaining non-hydrogen atoms were located on subsequent difference Fourier syntheses and refined anisotropically. Hydrogen atoms were calculated and fixed at 0.96 Å from carbon. At convergence: R_F = 4.81% and R_{wF} = 4.75%, GOF = 1.091, highest final difference peak, 0.68 e Å^{-3} (1.19 Å from Ru). SHELXTL (5.1) programs were used for all calculations (Nicolet Corp., Madison, WI).



1



2 M = Mo; R = Ph
3 M = Mo; R = ^{t}Bu
4 M = W; R = ^{t}Bu



5 R = H; X = X' = Cl
6 R = H; X = X' = Br
7 R = H; X = X' = I
8 R = H; X = Cl; X' = Br
9 R = Me; X = X' = Cl

and fractional atomic coordinates are presented in Table I. The cyclopropenyl ligand is η^3-bound to the ruthenium atom with the unique carbon C(6) directed away from the cyclopentadienyl ring. Like its Mo analogue **2**, but in contrast to the W complex **1**, the distance from Ru to the C_3 ring centroid [2.036 (8) Å] is significantly longer than that to the C_5 ring centroid [1.833 (8) Å], although both rings are closer to the metal than are their counterparts in **2** (vide supra). While the cyclopropenyl ring in **6** is held more closely to the metal than that in **2**, the phenyl rings in **6** (Figure 1) are bent back from the plane of the cyclopropenyl ring significantly less than those in **2**. Thus there is no direct correlation between closeness of binding (as measured by metal–ring centroid distances) and substituent bend-back angle.[3a,4b]

Spectroscopic analysis of **6** and its relatives indicated that the solid-state structure is maintained in solution.[7] In contrast to their fluxional relatives **2**–**4**, the presence of two ^{13}C resonances for the cyclopropenyl ring carbon atoms, and resonances due to two different phenyl groups, for complexes **5**, **6**, **7**, and **9** indicates a conformationally static structure in solution.[10] The observation of three cyclopropenyl ring carbon resonances for the mixed halo complex **8** is also consistent with conformational rigidity. That this increased rotational barrier is not due to steric interactions due to more closely bound cyclopentadienyl and cyclopropenyl rings is indicated by the free rotation of the cyclopentadienyl and pentamethylcyclopentadienyl rings, as evidenced by a single environment for all atoms in the ^{1}H and ^{13}C NMR spectra of **5**–**9**.

In summary, even though the cyclopropenyl ring is less closely bound to the metal center than is the cyclopentadienyl ring, the rotational barrier for the three-membered ring appears to exceed significantly that for the five-membered ring. The origin of the relatively high barriers in **1** and **5**–**9**, as compared to the low barriers in **2**-**4**,[10] must be related to the intimate details of orbital interactions between the respective metal fragments and the cyclopropenyl ring. It is hoped that molecular orbital calculations on the isoelectronic complexes **2** and **6** will allow further elucidation of these differences.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research (Grant AFOSR-86-0075), the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of our research. A generous loan of ruthenium trichloride from Johnson-Matthey Inc. is also gratefully acknowledged. We thank Dr. Paul Eagan for a preprint of ref 8a.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (4 pages); a listing of observed vs calculated structure factors (11 pages). Ordering information is given on any current masthead page.

---

[10] The smallest separation between cyclopropenyl carbon peaks ($\Delta\nu$) is 30 Hz for the mixed halide complex 8. Since the coalescence temperature is clearly >298 K, a *minimum* $\Delta G^* \geq 62$ kJ mol^{-1} for cyclopropenyl rotation can be calculated for this complex. Estimation of a value for 2 requires an estimate of $\Delta\nu$ at the slow exchange limit, which has not been reached at -80 °C.[3a] Assuming that $\Delta\nu$ for 2 is 3000 Hz (the value obtained for 6) and that the coalescence temperature is clearly <193 K leads to a *maximum* $\Delta G^* \leq 32$ kJ mol^{-1} for cyclopropenyl rotation in 2. It seems reasonable to conclude that the barriers for triphenylcyclopropenyl rotation in the Ru(IV) complexes are at least 30 kJ mol^{-1} greater than that in their isoelectronic molybdenum analogue.

Organobimetallic Complexes with $Hg(CH_2P(S)Ph_2)_2$. Syntheses and Characterization of Two Structural Isomers of $[HgAu(CH_2P(S)Ph_2)_2]PF_6$ and the Hg Precursor

Suning Wang and John P. Fackler, Jr.*

Department of Chemistry and
Laboratory for Molecular Structure and Bonding
Texas A&M University
College Station, Texas 77843

Received July 11, 1988

Summary: The ylide complex $Hg(CH_2P(S)Ph_2)_2$ (**1a**) has been synthesized. **1a** reacts readily with Au(THT)Cl (THT = tetrahydrothiophene) in CH_2Cl_2 in the presence of $TlPF_6$ to yield a new bimetallic compound with HgC_2 and AuS_2 bonding, $[HgAu(CH_2P(S)Ph_2)_2]PF_6$ (**2a**). This compound is isostructural with an isomer having AuSC and HgSC bonding, **3a**, obtained from the reaction of PPN[$Au(CH_2P(S)Ph_2)_2$] with $HgCl_2$ in the presence of $TlPF_6$. The structures of **1a**, **2a**, and **3a** were determined by single-crystal X-ray diffraction. **2a** and **3a** do not interconvert upon heating in THF.

Recently, we have reported the synthesis and structure of the (methylenethiophosphinate)gold(I) complex PPN-[$Au(CH_2P(S)Ph_2)_2$] and its use as a synthetic precursor for heterobimetallic methylenethiophosphinate complexes.[1-3] The complexes $Au_2Pt(CH_2P(S)Ph_2)_4$, $AuTl(CH_2P(S)Ph_2)_2$, and $Au_2Pb(CH_2P(S)Ph_2)_4$ were obtained. These heterobimetallic complexes display unique structural features and very interesting physical and chemical properties. The scarceness of Hg^{II}–Au^I bimetallic complexes and the chemical similarities of Au^I and Hg^{II} ions have promoted us to synthesize mercury–gold containing ylide bimetallic

---

[1] Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. *Organometallics* **1986**, *6*, 1932.

[2] Wang, S.; Fackler, J. P.; King, C.; Wang, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 3308.

[3] Wang, S.; Garzon, G.; Fackler, J. P., Jr.; King, C. K.; Wang, J. C. *J. Am. Chem. Soc.*, submitted for publication.

0276-7333/88/2307-2415$01.50/0