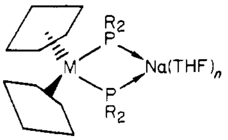
exchange limiting spectrum (presumably two doublets) was not obtained, at −126 °C IIe exhibits two broad ($\Delta\nu_{1/2} \simeq$ 700 Hz) resonances at 270.2 and −15.3 ppm,[17] *a chemical shift difference of 285 ppm for two PCy_2 ligands on the same metal.* These two resonances coalesce at −100 °C, corresponding[18] to an activation energy of 6.0 ± 0.2 kcal/mol.

Reduction of complexes IIa–f by sodium naphthalenide in THF at 25 °C produces the thermally stable Zr^{III} and Hf^{III} complexes $[(\eta\text{-}C_5H_5)_2M(PR_2)_2][Na(THF)_n]$, IIIa–f, as determined by ESR spectroscopy.[19–21] The four-membered, inorganic ring structure shown is suggested by the ^{23}Na hyperfine splitting observed in the ESR spectra of complexes IIIa,b. Although complexes IIIa–f are presumably isostructural, ^{23}Na hyperfine splittings were not observed for R = Ph and not resolved for M = Hf, because of the large inherent line widths ($\Delta\nu_{1/2} \simeq$ 0.5 mT). Complexes IIId–f are the most thermally stable organohafnium(III) species yet reported;[22] the ESR signal persists for days at room temperature.



IIIa, M = Zr, R = Et
b, M = Zr, R = Cy
c, M = Zr, R = Ph
d, M = Hf, R = Et
e, M = Hf, R = Cy
f, M = Hf, R = Ph

Further details of these new metal-containing diphosphines will appear in a subsequent full paper.[9]

Acknowledgment. We wish to thank the following persons for fine technical assistance in the following areas: synthesis, D. W. Reutter, K. H. Richmond, W. M. Gray, and S. A. Hill; X-ray, L. F. Lardear; NMR, J. D. Center, G. Watunya, Drs. D. W. Ovenall, P. J. Domaille, and D. C. Roe; ESR; D. J. Jones and Dr. P. J. Krusic.

Registry No. IIa, 86013-23-2; IIb, 86013-24-3; IIc, 86013-25-4; IId, 86013-26-5; IIe, 86013-27-6; IIf, 86013-28-7; IIIa, 86013-29-8; IIIb, 86013-30-1; IIIc, 86013-31-2; IIId, 86013-32-3; IIIe, 86013-33-4; IIIf, 86013-34-5; $(\eta\text{-}C_5H_5)_2ZnCl_2$, 1291-32-3; $(\eta\text{-}C_5H_5)_2HfCl_2$, 12116-66-4; $LiPEt_2$, 19093-80-2; $LiPCy_2$, 19966-81-5; $LiPPh_2$, 4541-02-0; sodium naphthalenide, 3481-12-7.

Supplementary Material Available: Tables of final fractional atomic coordinates, bond distances and angles, and observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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(17) ^{31}P NMR chemical shifts are positive downfield from external 85% H_3PO_4.

(18) Martin, M. L.; Martin, G. J.; Delpeuch, J.-J. "Practical NMR Spectroscopy"; Heyden: Philadelphia, 1980; Chapter 8, p 339.

(19) Although we have been unable to crystallize IIIa–f, no other products are detected by ESR or NMR spectroscopy. Comparison of the doubly integrated ESR signal intensities vs. external DPPH in THF indicates that the reductions are quantitive within the experimental error of ca. 20%.

(20) 9.54-GHz ESR data at 25 °C in THF: (g_{av}, $a(^{31}P)$ in mT): IIIa, 1.9902, 1.00, $a(^{91}Zr) \simeq$ 2.0, $a(^{23}Na)$ = 0.18; IIIb, 1.9872, 1.23, $a(^{91}Zr) \simeq$ 2.4, $a(^{23}Na)$ = 0.20; IIIc, 1.9860, 1.14, $a(^{91}Zr) \simeq$ 2.3; IIId, 1.9753, 1.10; IIIe, 1.9666, 1.28; IIIf, 1.9653, 1.24.

(21) The low-temperature ESR spectra of complex IIIc and several titanium analogues (generated from $(\eta\text{-}C_5H_5)_2MCl_2$ and excess $NaPR_2$) have been reported previously.[7]

(22) Lappert, M. F.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1980**, 1284.

Metal vs. Ligand Exchange upon Reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ with $(\mu_3\text{-}S)Co_3(CO)_7LX$ Clusters. A Two-Step Synthesis of the Optically Active Cluster $(\mu_3\text{-}S)Mo(\eta^5\text{-}C_5H_5)Co_2(CO)_6[\mu\text{-}1,2\text{-}\eta^2\text{-}C(R^1)N(R^2)]$

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Received March 11, 1983

Summary: The $(\mu_3\text{-}S)Co_3(CO)_7LX$ clusters react with $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ to afford either $(\eta^5\text{-}C_5H_5)Mo(CO)_2LX$ complexes or the heteronuclear cluster $(\mu_3\text{-}S)Mo(\eta^5\text{-}C_5H_5)Co_2(CO)_6LX$, depending on the ability of the bridging ligand to stabilize the binuclear intermediates. The X-ray structure analysis of the $MoCo_2$ cluster shows that it spontaneously forms optically active crystals. The catalytic activities of four clusters in hydroformylation have been examined.

Transition-metal cluster compounds constitute an area of organometallic chemistry currently under intense investigation, largely due to their potential utilization in homogeneous catalysis where they can function either as the catalytically active species or may serve as precursors for the release of reactive fragments.[1–3] Concerning the latter point it may be noted that most of the known clusters are composed of individual fragments linked by metal–metal bonds with the occasional participation of other elements (carbon, sulfur, phosphorus, ...) bonded to the metal atoms. The ability of clusters to act as catalysts has been debated, and although plausible mechanisms have been proposed,[2] definitive proof that they can be active as a structural whole does not seem to have been obtained.[4] This has led to considerable efforts directed toward the synthesis of optically active clusters[5] which would be suitable species with which to examine the process of optical induction in cluster-catalyzed reactions because such intrinsically chiral compounds should provide the proof that clusters considered as an entity can be catalytically active.

Our approach to the synthesis of chiral clusters was based on the discovery that chirality could be obtained directly by treating with $Co_2(CO)_8$ compounds such as $R^1C(S)NR^2R$.[3] With secondary thioamides[6] ($R^1 \neq R^2 \neq$ H, R^3 = H), thiocarbonyl chloride[7] (R^1 = Cl, $R^2 = R^3$ = Me) and primary thioamides[8] ($R^1 \neq$ H, $R^2 = R^3$ = H),

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(1) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

(2) Pittman, C. U., Jr.; Ryan, R. C. *Chem. Tech* **1978**, 170.

(3) Geoffroy, G. L. *Acc. Chem. Res.* **1980**, *13*, 469.

(4) Whyman, R. "Transition Metal Clusters"; Johnson B. F. G., Ed.; Wiley: New York, 1980; Chapter 8.

(5) (a) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 531. (b) *Ibid.* **1980**, *19*, 65. (c) Beurich, H.; Vahrenkamp, H. *Ibid.* **1981**, *20*, 98.

(6) Patin, H.; Mignani, G.; Mahé, C.; Le Marouille, J. Y.; Benoît, A.; Grandjean, D.; Levesque G. *J. Organomet. Chem.* **1981**, *208*, C39.

(7) Mahé, C.; Patin, H.; Benoît, A.; Le Marouille, J. Y. *J. Organomet. Chem.* **1981**, *216*, C15.

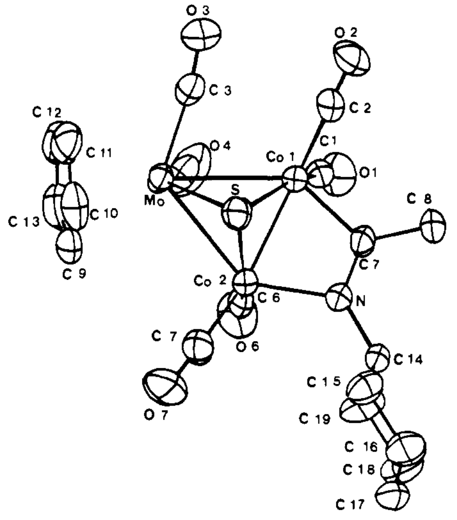
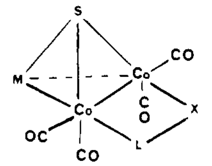


Figure 1. Perspective ORTEP drawing of cluster **7**. Average values of the most relevant bond lengths (Å) and angles (deg) which their esd's are as follows: Co(1)–Mo = 2.776 (1); Co(2)–Mo = 2.773 (1); Co(1)–Co(2) = 2.426 (1); Mo–S = 2.370 (2); Co(1)–S = 2.165 (2); Co(2)–S = 2.184 (2); Co(1)–C(7) = 1.950 (6); Co(2)–N = 2.003 (5); C(7)–N = 1.267 (9); Co(1)–Mo–Co(2) = 51.85 (3); Mo–Co(1)–Co(2) = 64.02 (3); Mo–Co(2)–Co(1) = 64.13 (3).

clusters **1**, **2**, and **3**, respectively, were obtained in good yield.



The use of (*R*)-(–)-PhC(S)NHCH(Ph)CH_3, **4**, produced cluster **1** as a mixture of diastereoisomers which could be partially separated by fractional crystallization,[9] unfortunately we were unable to obtain intrinsically chiral clusters by racemizing the asymmetric carbon atom of the bridging ligand. We then examined the possibility of replacing the cobalt tricarbonyl grouping by other organometallic fragments. This reactivity pattern can be understood in terms of the isolobal relationship, a concept elegantly developed by Hoffman and co-workers.[10] However as illustrated by the following examples, the success of such replacement may depend dramatically on the relative abilities of the bridging ligand to stabilize the bimetallic intermediate or to be removed.

Upon reaction with $CpMo(CO)_3^-$, prepared in anhydrous THF under argon, two different types of behavior of our clusters were observed. Clusters **2** and **3** gave rise to ligand exchange, affording the molybdenum complexes **5** and **6**, $(\eta^5\text{-}C_5H_5)Mo(CO)_2L$[**5**, L = (1,2-$\eta^2$-S–C–$NMe_2$); **6**, L = (1,3-$\eta^2$-S–C($R^1$)–NH)]. In contrast, with cluster **1** replacement of $Co(CO)_3$ by $CpMo(CO)_2$ was successful and the heteronuclear cluster **7** was obtained. Structures **5**–**7** were assigned on the basis of elemental analysis, mass spectroscopy, and other spectroscopic information.[11] It is noteworthy that metal exchange occurs exclusively with cluster **1** for which the shortest metal–metal distance has been recorded.[6,8] The success of metal exchange thus appears to depend dramatically on the stability of the binuclear intermediate which seems to be enhanced when the bridging ligand imposes a strong geometrical constraint. The X-ray structure analysis of **7** showed that it spontaneously forms optically active crystals.[14] The perspective view presented in Figure 1 corresponds to one enantiomer. Large crystals of **7** were separated by manual selection. Their circular dichroism curves prove that both enantiomers have been obtained.[16]

In order to check the catalytic properties of our clusters, the hydroformylation of styrene was studied.[17] Clusters **1** and **3** are effective catalysts with respective conversions of 25 and 16%, the ratio of branched to linear aldehydes being 60/40. Clusters **2** and **7** did not yield any detectable hydroformylation products. In all cases only a small amount of the organometallic compounds can be recovered. These results demonstrate that only those clusters which effectively catalyze the hydroformylation of styrene possess a $Co(CO)_3$ grouping which can be liberated during a fragmentation process. The most striking fact is that replacement of cobalt in cluster **1** by molybdenum results in complete loss of catalytic activity. It seems to us that the approach to proving the reality of the catalytic activity of clusters by studying asymmetric synthesis promoted by an intrinsically chiral cluster may not be the ideal route. Our results are more likely in agreement with the concept of clusters acting as storehouses for the release of catalytically active fragments.

Acknowledgment. We acknowledge support by the CNRS and the DGRST for grants to C.M. and A.B.

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(8) Benoît, A.; Darchen, A.; Le Marouille, J. Y.; Mahé, C.; Patin, H. *Organometallics* **1983**, *2*, 555.

(9) To 0.05 mol of (*R*)-(+)-α-methylbenzylamine in 30 mL of CH_2Cl_2 was added 0.05 mol of PhC(S)SCH_3; after 48 h at room temperature the mixture was chromatographed on silica to afford **4** in 75% yield (oil); $[\alpha]^{20}{}_D$ -194° ($CHCl_3$, *c* 0.0126 g/cm³). By the published procedure[6] cluster **1** (oil) was obtained in 62% yield: ^1H NMR δ 1.36 (d, *J* = 6 Hz) and 1.30 (d, *J* = 6 Hz) for the diastereotopic methyls in 1/1 ratio ($CDCl_3$, Me_4Si, 80 MHz). From ethanol–acetone a compound, mp 103–104 °C, was obtained: ^1H NMR δ 1.36 (d, *J* = 6 Hz, 85%) and 1.30 (d, *J* = 6 Hz, 15%).

(10) (a) Elian, M.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffman, R. *Ibid.* **1976**, *15*, 1148. (c) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(11) **5**: 34%; mp 112 °C (lit.[12] 111 °C); $C_{10}H_{11}NO_2SMo$, M^+ 306.9504 (calcd), 306.9558 (found). **6** (R^1 = Ph): 85%; mp 171 °C; $C_{14}H_{11}NO_2SMo$, $M^+ - 2CO$ 298.9666 (calcd), 298.9672 (found); IR (Nujol) ν_{CO} 1840, 1940 cm^{-1}; ^1H NMR δ 7.53 (5 H), 5.63 (5 H), 2.03 (1 H). Anal. Calcd: C, 47.59; H, 3.12; N, 3.96; S, 9.06; Mo, 27.19. Found: C, 47.25; H, 3.32; N, 4.11; S, 8.73; Mo, 27.25. Similar compounds can be obtained[13] by reaction of $CpMo(CO)_3Cl$ with $R^1NHC(S)CH_3$. **7** ($R^1 = CH_3$, $R^2 = C_6H_{11}$): 62%; mp 145–148 °C; $C_{19}H_{19}NO_6SCo_2Mo$, $M^+ - CO$ 576.8701 (calcd), 576.8686 (found); IR (Nujol) ν_{CO} 2080–1980 cm^{-1}; ^1H NMR δ 5.32 (5 H), 2.39 (3 H), 1.40 (11 H). Anal. Calcd: C, 37.81; H, 3.15; N, 2.32; S, 5.31; Co, 19.57; Mo, 15.92. Found: C, 37.67; H, 3.09; N, 2.03; S, 4.97; Co, 20.14; Mo, 15.59.

(12) Dean, W. K.; Treichel, P. M. *J. Organomet. Chem.* **1974**, *66*, 87.

(13) Bernal, I.; Reisner, G.; Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1977**, *137*, 329.

(14) Convenient single crystals of **7** were obtained from hexane. Crystal data for complex **7** are as follows: space group $P_{2_12_12_1}$; $Z = 4$; $a = 8.594$ (1) Å, $b = 11.434$ (3) Å, $c = 22.823$ (5) Å; $\alpha = 90.0$ (0)°, $\beta = 90.0$ (0)°, $\gamma = 90.0$ (0)°. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares procedures: $R = 0.026$ and $R\omega = 0.034$ using 1937 reflections with $I > 2\sigma(I)$. All the structural calculations were performed on a PDP 11/60 computer with the SDP package.[15]

(15) B. A. Frenz, 1978, in M. Schenk and R. Olthof-Hazekamp (Eds.), Enraf-Nonius CAD4-SDP, a real-time system for concurrent X-ray data collection and crystal structure determination. Computing in Crystallography.

(16) $[\alpha]^{21}{}_{407} = -225° \pm 25$ ($CHCl_3$, *c* 4.10^{-5} g/cm³), Δε(407 nm) = –3.9; $[\alpha]^{21}{}_{407} = +395° \pm 25$ ($CHCl_3$, *c* $7.6.10^{-5}$ g/cm^{-3}), Δε(407 nm) = +4.

(17) An autoclave Engineers AFP-305 (300 mL) with magnetic drive was charged with 50 mL of distilled THF, 10 g of styrene, and 0.1 g of cluster. Conditions: total pressure of CO + H_2 120 atm, 8 h at 130 °C (at temperatures lower than 110 °C no hydroformylation was observed). Analysis of the reaction mixtures were done by gas chromatography techniques. Removal of the majority of the organic products by distillation under reduced pressure followed by chromatography of the residue on silica plates allowed us to recover small quantities of clusters **1**, **3**, and **7** (respective amounts 12%, 7%, 15%). Cluster **2** could be expected to show some catalytic activity according to the fact that it possesses a $Co(CO)_3$ grouping; its great thermal instability (no recovery) may ensure that it is completely destroyed before the catalytic process is initiated.

Registry No. 1, 78823-94-6; 2, 79161-14-1; 3, 84432-84-8; 4, 86022-50-6; 5, 37035-38-4; 6, 85976-72-3; 7, 85976-73-4; PhC(S)SCH$_3$, 2168-78-7; Co$_2$(CO)$_8$, 10210-68-1; (*R*)-(+)-α-methylbenzylamine, 3886-69-9; styrene, 100-42-5.

Supplementary Material Available: Listing or positional and thermal atomic parameters and experimental and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Iron Complexes of Homocycloheptatrienylidene

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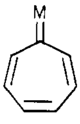
Received September 7, 1982

Summary: Protonation of FpCOT and FppCOT (Fp = η^5-cyclopentadienyl)iron dicarbonyl, COT= cyclooctatetraene, Fpp = (η^5 - cyclopentadienyl)iron carbonyl tri-R-phosphine) with strong acid produces homoaroamtic carbene complexes **7**, **8**, and **9**. Although all three complexes are clearly homoaromatic, ^{1}H and ^{13}C NMR spectra suggest that dπ–pπ back-bonding reduces the homoaromaticity relative to the parent homotropylium ion.

In previous papers[1-3] we have reported the preparation and properties of some transition–metal complexes of cycloheptatrienylidenes **1–3**. As a continuation of our efforts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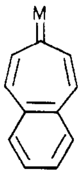
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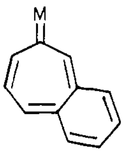
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directed toward the synthesis and properties of complexes of cyclic conjugated carbenes that are stabilied by incorporation of the carbene p orbital in an aromatic pπ orbital system,[4] we have now prepared three iron complexes of homocycloheptatrienylidene. In this communication we report the synthesis of **7–9** (Scheme I) and spectral properties that both elucidate their structures and show that while considerable homoaromaticity is retained in the organic ligands of each complex, there is also significant back-bonding from iron into the π system.

The method of synthesis of the three complexes is outlined in Scheme I.[6] Neither of the two methods used to prepare FpCOT (**4**) gave very high yields (ca. 15–29%). However, of the two, we found the high dilution addition of Fp$^-$ to BrCOT at 21 °C to be generally more satisfactory because it not only gave somewhat better yields but was easier to workup. σ complexes **5**[9] and **6**[10] were made in high yield by photoinduced replacement of CO by R$_3$P. The carbene complexes were made by protonation of the corresponding σ complexes (−40 °C) with either excess dry HCl, 2 equiv of FSO$_3$H, or 2 equiv of CF$_3$CO$_2$H in dry CH$_2$Cl$_2$,[11] Addition of 1.1 equiv of Ph$_2$C$^+$PF$_6^-$ followed by dilution with cold, dry ether gave the carbene complexes as their PF$_6^-$ salts.[12]

The hexafluorophosphate salt **7**[13] crystallized as orange needles which are stable in air below −10 °C but which rapidly react with oxygen in solution. Above −10 °C it

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(1) Allison, N. T.; Kawada, Y.; Jones, W. M. *J. Am. Chem. Soc.* **1978**, *100*, 5224.

(2) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 2452.

(3) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *21*, 1321.

(4) The first complexes stabilized by aromaticity were cyclopropenylidene complexes, first synthesized by Ofele and his co-workers.[5]

(5) (a) Ofele, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 950. (b) Ofele, K. *J. Organomet. Chem.* **1970**, *22*, C9.

(6) Bromocycloctatetraene was prepared by the method of; Gasteiger, J.; Gleam, G. E.; Huisgen, R.; Konz, W. E.; Schneeg, U. *Chem. Ber.* **1971**, *104*, 2412. KFp was prepared by the method of Gladysz.[7]

(7) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1.

(8) (a) **4** has been previously prepared via the cyclooctatetraenyllithium route. Cooke, M.; Russ, C. R.; Stone, F. . A. *J. Chem. Soc., Dalton Trans.* **1975**, 256. For example of displacement of a vinyl fluoride by Fp$^-$, see: King, R. B.; Bisnette, M. B., *J. Organomet. Chem.* **1964**, 2, 38. (b) **4** is a yellow air-sensitive oil (best stored refrigerated in solvent other than CHCl$_3$): ^{1}H NMR (300 mHz, CD$_2$Cl$_2$, δ) 4.81 (s, Cp) 5.22 (dd, H7, $J_{7,8}$ = 11.1 Hz, $J_{2,3}$ = 3.4 Hz), 5.51 (dd, H5, $J_{5,6}$ = 10.9 Hz, $J_{4,5}$ = 3.2 Hz), 5.68 (d, H2, $J_{2,3}$ = 2.8 Hz), 5.75 (dd, H6), 5.77–5.85 (m, H3 and H4), 6.16 (d, H8); ^{13}C NMR (CD$_3$COCD$_3$, δ) 87.2 (Cp), 119.3, 129.2, 132.6 (2 C), 136.7, 139.3, 147.7, 151.7 (C1), 217.2 (CO), 217.7 (CO); IR (film, cm^{-1}) 2960, 1990, 1925, 1560, 1400, 1005, 909, 827, 702, 714; high-resolution mass spectrum, *m/e*(calcd) 280.018 50, *m/e*(measd) 280.019 84; Anal. Calcd for C$_{15}$H$_{13}$FeO: C, 64.31; H, 4.32. Found: C, 64.07; H, 4.40. The isodynamic interconversions of the COT moiety in **4** were observed. Exchange of diastereotopic CO ligand signals (^{13}C NMR) allowed calculation of ΔG^*(ring inversion) = 16.6 kcal/mol; broadening and coalescence of the COT ^{1}H NMR signals due to bond shift processes was consistent with a ΔG^*(bond shift) ~18 kcal/mol.

(9) FppCOT's were prepared by photolysis of **4** in THF (overnight) with the appropriate phosphine using a 450-W Hanovial Hg lamp. **5** was isolated by short column chromatography (neutral alumina, hexane) and is an air-stable orange glass: ^{1}H NMR (300 mHz, CD$_2$Cl$_2$, δ) 4.45 (d, Cp of one diastereoisomer, J_{PH} = 1.1 Hz) 4.49 (d, Cp of other diastereoisomers, J_{PH} = 1.1 Hz) 4.91 (dd, H7, $J_{7,8}$ = 11.1 Hz, $J_{6,7}$ = 3.2 Hz), 4.95 (dd, H7′, $J_{7',8'}$ = 11.0 Hz, $J_{6',7'}$ = 3.2 Hz), 5.30–5.84 (complex multiplet H2, H5, H6, H4, H3), 6.10 (dd, H8), 6.29 (dd, H8′), 7.37 (br s, phenyls); ^{13}C NMR (CD$_2$Cl$_2$, δ) 85.4 (pseudo d, Cp diastereoisomers) 116.6 (pseudo d), 130–140 (phenyl and COT), 149.5 (s) 164.4 (pseudo dd, C-1 of COT) 222.3 (pseudo dd, CO); IR (CHCl$_3$, cm^{-1}) 2995, 1920; mass spectrum, *m/e* 486 (M$^+$ − CO), 383, 262 (100%), 224, 121, 56; *Anal.* Calcd for C$_{32}$H$_{27}$FeOP: C, 74.72; H, 5.29. Found: C 74.49; H, 5.35. The isodynamic interconversions of the COT moiety in **5** were observed. Exchange of diastereotopic Cp signals (^{1}H NMR) allowed calculation of ΔG^* (ring inversion) = 17.3 kcal/mol; broadening and coalescence of the COT H NMR signals due to bond shift processes produced a $\Delta G^* \sim$ 18 kcal/mol.

(10) **6** is a yellow-orange air-sensitive oil: ^{1}H NMR (300 mHz, CD$_3$COCD$_3$, δ) 0.9–1.9 (complex m, butyl), 4.4 and 4.5 (d's, Cp diastereoisomers, J_{PH} = 1.1 Hz), 4.9 (m, H7), 5.3 (m, H5), 5.6 (complex m, H2, H6, H3, H4), 6.3 (m, H8); ^{13}C NMR (CD$_3$COCD$_3$, δ) 24–32 (butyl) 3.6 (pseudo d, Cp diastereoisomers), 115.7 (pseudo d), 132.0 (s), 133.3 pseudo d), 137.0 (2 C, separated below 0 °C), 149.9 (pseudo d) 167.1 (pseudo dd, C1 of COT), 221.9 (pseudo dd, CO); IR^1 (CHCl$_3$, cm^{-1}) 2995, 1925. The isodynamic interconversions of the COT moiety in **6** were observed. Exchange of diastereoisomeric Cp signals (^{1}H NMR) allowed calculation of ΔG^*(ring inversion) = 17.0 kcal/mol; broadening and coalescence of the COT ^{1}H NMR signals due to bond shift processes produced a $\Delta G^* \sim$ 18 kcal/mol.

(11) Both **5** and **6** showed NMR spectra indicative of mixtures of slowly interconverting diasteroisomers.[9,10] It was therefore quite a surprise that in neither case did the protonated products appear as diastereomers. For instance, in the ^{13}C NMR spectra, in each case the carbonyl resonance appeared as simple doublets (coupled with phosphorus), in the ^{1}H spectra the exo and endo hydrogens appeared as simple doublets, etc. This surprising result is probably due to thermodynamic preference for one diastereoisomer which is rapidly formed (by a ring-flipping process) from a mixture of initially produced diastereoisomers. neither **8** nor **9** showed any significant change in their NMR spectra with changes in temperature.

(12) We have found metathesis with Ph$_3$C$^+$PF$_6^-$ to be a convenient technique for exchanging anions in relatively nonpolar solvents due to the solubility of the resulting Ph$_3$CX.

(13) **7**: ^{1}H NMR (300 mHz, CD$_2$Cl$_2$, −20 °C, δ) 1.27 (t, H8$_{endo}$ $J_{8_{endo},8_{exo}}$ = 8.9 Hz, $J_{7,8_{endo}}$ = 0.0 Hz), 5.26 (s, Cp), 5.57 (t, H8$_{exo}$ = 7.3 Hz), 5.78 (t, H7, $J_{6,7}$ = 9.0 hZ), 7.34 and 7.35 (m, H4 and H3, $J_{3,4}$ = 9.1 Hz), 7.47 (t, H6, $J_{5,6}$ = 6.9 Hz), 7.83 (m, H5, $J_{4,5}$ = 11.4 Hz), 8.86 (d, H2, $J_{2,3}$ = 9.7 Hz, $J_{2,5}$ = 0.9 Hz); ^{13}C NMR (CD$_2$Cl$_2$, −20 °C δ) 210.4 (CO), 211.5 (CO), 269.0 (C1); IR (KBr, cm^{-1}) 2002, 1970, 1440, 1300, 1275, 1070, 980, 840 cm^{-1}; mp (rapid heating), orange to brown at 70 °C melts at ca. 80 °, effervesces at 100–105 °C.

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