the 3:3:1 structures are transition states, are somewhat high, though the correct ordering of H and Cl barriers is obtained. It could be that the approximate computational method is at fault. We suspect that more of the discrepancy stems from the fact that our idealized 3:3:1 structures are still far from the true transition state or intermediate structures. We have not optimized these geometries nor considered more asymmetric pseudo-seven-coordinate pathways. This remains a project for the future.

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Appendix

Our calculations were of the extended Hückel type,[24] with "weighted" H_{ij}'s. The parameters are listed in Table IV. The H_{ii} values of V and Mo were obtained by charge iterative calculations on $CpV(CO)_4$ (experimental geometry) and $CpMo(CO)_3CH_3$ (geometry of the ethyl complex).

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[24] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397-1412. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179-2195; **1962**, *37*, 2872-2883.

[25] Ammeter, J. H.; Burgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686-3692.

Dehydrogenation of 1,3-Cyclohexadiene by $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. Preparation, Dynamic NMR, and X-ray Crystal Structure of $[\eta^3\text{-}CH_2C_6(CH_3)_5]Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$

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The coordinately unsaturated rhodium hydride dimer, $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, effected a dehydrogenation of 1,3-cyclohexadiene to benzene. This reaction was not catalytic; the other product was (η^3-cyclohexenyl)rhodium bis(triisopropyl phosphite). In attempts to follow the 1,3-cyclohexadiene reaction along a back-reaction sequence, the chemistry of $(\eta^6\text{-arene})Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$ was examined. Reaction of the benzene complex with potassium triisopropoxyborohydride gave benzene and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. Reaction of the hexamethylbenzene complex with either methyllithium or potassium triisopropoxyborohydride gave (η^3-pentamethylbenzyl)rhodium bis(triisopropyl phosphite). The latter compound was crystallographically and spectroscopically defined. NMR studies established that this molecule exists in rapid equilibrium with an excited-state form proposed to be an (η^5-benzyl)rhodium structure.

Introduction

Synthesis and chemistry of coordinately unsaturated polynuclear transition-metal complexes represent a major focus of our research. Previously, we have described the synthesis[2,3] and the structural features[2,4-6] of $[HRhL_2]_x$ clusters and have also demonstrated the high reactivity of these polynuclear compounds to catalytic olefin and alkyne hydrogenation reactions.[3,7-9] To date, the major set of clusters studied has been the phosphite complexes, $\{HRh[P(OR)_3]_2\}_x$, particularly the dimeric species $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.

Reactivity toward donor molecules under stoichiometric conditions was high for the coordinately unsaturated hydride $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.[10,11] Nevertheless, there was significant selectivity to this reactivity. For example, the dimeric hydride reacted with 1 equiv of carbon monoxide or an acetylene to form $(\mu\text{-}H)_2(\mu\text{-}CO)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$[10] and $(\mu\text{-}H)(\mu\text{-}CR{=}CHR)Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$,[9] respectively. Simple donor molecules like phosphite elicited rapid cleavage of the dimeric form to generate the saturated mononuclear $HRhL_4$ species.[3] However, olefins reacted only very slowly, if at all, with the dimer.[12] Hydrogen oxidatively added to the dimer in an extremely fast reaction to form the triply bridged dimeric hydride.[13]

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[2] Day, V. W.; Fredrich, M. F.; Reddy, G. S.; Sivak, A. J.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 8091.

[3] Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

[4] Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2099.

[5] Brown, R. K.; Williams, J. M.; Sivak, A. J.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 370.

[6] Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1806.

[7] Muetterties, E. L.; Sivak, A. J.; Brown, R. K.; Williams, J. W.; Fredrich, M. F.; Day, V. W. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 487.

[8] Muetterties, E. L. *Catal. Rev.-Sci. Eng.* **1981**, *23*, 69.

[9] A mechanistic study of alkyne hydrogenations has been completed; Burch, R. R.; Muetterties, E. L., manuscript in preparation.

[10] Burch, R. R.; Muetterties, E. L.; Schultz, A. J.; Gebert, E. G.; Williams, J. M. *J. Am. Chem. Soc.*, **1981**, *103*, 5517.

[11] Burch, R. R.; Muetterties, E. L., unpublished results.

[12] These reaction rates are comparable to the rate of decomposition of the dimer in solution. Rates were very low; reaction time of days were required. Reaction products were complex and included alkanes apparently generated from the isopropyl groups in the phosphite ligands.

[13] Olefins do react with this hydride to form alkanes and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$; reaction rates are extremely high.

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$$H_2 + \{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2 \rightleftharpoons H[(i\text{-}C_3H_7O)_3P]_2Rh(\mu\text{-}H)_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$$

It was this ability of the dimer to react so readily with hydrogen that suggested that the dimer could be used to extract hydrogen from organic molecules with activated carbon–hydrogen bonds and that forms the basis for the studies discussed in this report.

Results and Discussion

1,3-Cyclohexadiene reacted with the coordinately unsaturated dimer, $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, to produce benzene and a monomeric complex, (η^3-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$, derived from fragmentation of the dimer.

$$3C_6H_8 + \{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2 \rightarrow H_2 + C_6H_6 + 2(\eta^3\text{-}C_6H_9)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2 \quad (1)$$

A careful analysis established the reaction to be stoichiometric and not catalytic: 1 equiv of benzene was formed per 1 equiv of rhodium dimer. Neither cyclohexane nor cyclohexene was detected, demonstrating that this reaction was *not* a disproportionation of 1,3-cyclohexadiene but simply a dehydrogenation of 1,3-cyclohexadiene to benzene.

The reactivity of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ toward 1,3-cyclohexadiene was high compared to olefins or other dienes and low compared to hydrogen, carbon monoxide, or dialkylacetylenes. Reaction with the latter set of compounds was nearly instantaneous.[3,9,10] Whereas reaction with olefins and most other dienes, including 1,4-cyclohexadiene, was very slow,[12,14] the reaction with 1,3-cyclohexadiene was complete within 3 h at 20 °C, in toluene or pentane solutions. Neither cyclohexene nor cyclohexane was dehydrogenated, by the rhodium dimer, to form benzene.

(η^3-Cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$, the other reaction product, was obtained as yellow crystals in 60% isolated yield. By spectroscopic (NMR) measure, the yield of this complex was quantitative. The identity of this rhodium complex was established by elemental analysis, mass spectrometry, and NMR spectroscopy. All ^{31}P and ^1H NMR data were fully consistent with a square-planar coordination geometry for the framework. Both the ^1H and the ^{31}P NMR spectra were temperature invariant; thus, there was no fast (NMR time scale) exchange processes *detectable* for this allylic complex in the solution state.

The tetrahydride $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$, formed from the H_2 reaction with the rhodium dimer, was also reacted with 1,3-cyclohexadiene. In this case, no benzene, cyclohexene, or cyclohexane was detected by gas chromatography. (η^3-Cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ was the major, if not exclusive, metal-containing product. This result suggests that the tetrahydride was produced from the reaction of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ and 1,3-cyclohexadiene and that it is the tetrahydride which reacts with 1,3-cyclohexadiene to ultimately yield (η^3-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$. NMR monitoring of the reaction of the dimer with the diene showed the gradual appearance of both benzene and (η^3-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ at comparable rates; no intermediates could be detected. These results are summarized in Figure 1. One implication of the proposed reaction scheme in Figure 1 is that if two hydrogen atoms from the $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ species produced in the dehydrogenation step (Figure 1) were captured by some reagent so as to selectively reform the dimer,[15] then the reaction would be a catalytic dehydrogenation of cyclohexadiene to benzene (a so-called catalytic hydrogen-transfer reaction[16]). Since the reactivity of $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ toward terminal olefins is exceedingly high, 1-hexene was examined as a hydrogen "trap" (to give hexane). In fact, the yield of benzene in the dimer–cyclohexadiene reaction was increased by the presence of 1-hexene but because the rates of reaction of the hexene and the cyclohexadiene with $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ are comparable, the yield of benzene was raised only to 1.84 equiv per rhodium dimer.

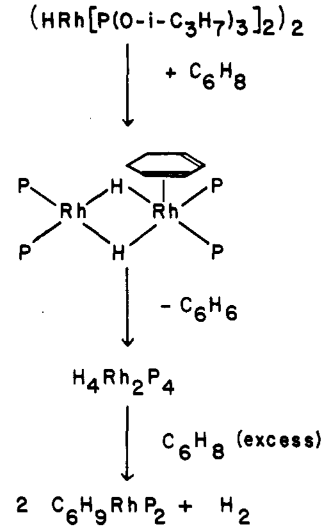

Figure 1. Scheme showing the reaction of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ with 1,3-cyclohexadiene to yield benzene and $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$. Subsequent reaction of the tetrahydride with additional 1,3-cyclohexadiene to give (η^3-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ and hydrogen was independently demonstrated to be a fast reaction.

Under 1 atm of hydrogen, (η^3-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ reacted rapidly in pentane solution to produce $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ and equivalent amounts of cyclohexene and cyclohexane. Spectroscopically, the time required to completely effect scission of the $Rh\text{–}C_6H_9$ bond was on the order of minutes at 20 °C, but longer time periods were usually employed to ensure complete recombination of the rhodium fragments to form the dimer. This behavior is similar to that for other compounds of the general formulation (η^3-C_3R_5)Rh[phosphite]$_2$.[3] Although the hydrogenolysis was quantitative in pentane, the reaction in toluene proceeded along a different pathway to produce cyclohexane, cyclohexene, and methylcyclohexane in a 10:1:3 molar ratio (after 24 h) and a nonhydridic rhodium species. The identity of this species remains uncertain because it was intractable. Initially, we thought that this complex was an intermediate complex to the final hydrogenation products of cyclohexane and the rhodium dimeric hydride. On the basis of the chemistry established for such rhodium and cobalt species, hydrogen should convert such an intermediate to the cycloalkane. However,

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(14) 1,5-Cyclooctadiene appears to be an exception to this. Burch, R. R.; Muetterties, E. L.; Day, V. W., unpublished results.

(15) Alternatively, hydrogen could be evolved above the reaction solution to regenerate $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.

(16) Examples of the catalytic hydrogen-transfer reaction include the disproportionation of cyclohexadiene to benzene and cyclohexene,[17] and the transfer of hydrogen from alcohols, ether, or formic acid to ketones or olefins.[18]

(17) Lyons, J. E. *Chem. Commun.* **1969**, 564. Moseley, K.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2884. Datta, S.; Wreford, S. S.; Beatty, R. P.; NcNeese, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1053. See also references cited therein.

(18) Gullotti, M.; Ugo, R.; Colonna, S. *J. Chem. Soc. C* **1971**, 2652. Vol'pin, M. E.; Kukolev, V. P.; Chernyshev, V. O.; Kolomnikov, I. S. *Tetrahedron Lett.* **1971**, 4435. Masters, C.; Kiffen, A. A.; Visser, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 1357. Nishiguchi, T.; Tachi, K.; Fukuzumi, K. *J. Org. Chem.* **1975**, *40*, 237. See also references cited therein.

no reaction of this nonhydridic complex with hydrogen was observed in either pentane or toluene solution.

In principle, the hydrogen produced in the reaction of the conjugated cyclohexadiene with the dimeric rhodium hydride could convert the reaction into a catalytic disproportionation because (η^3-cyclohexenyl)Rh[P(O-*i*-$C_3H_7)_3]_2$ undergoes hydrogenolysis, as discussed above. However, it is the very low hydrogen pressure resulting from the reaction of the conjugated cyclohexadiene with the dimer that effectively prevents a catalytic disproportionation pathway (the tetrahydride undergoes a fast, reversible dissociation of hydrogen at 20 °C).

Related compounds of formulation (η^3-cyclohexenyl)-Co[P(OR)$_3]_2$ and (η^5-cyclohexadienyl)Co[P(OR)$_3]_2$ have been postulated as intermediates in the catalytic hydrogenation of arenes by the catalyst precursor (η^3-C_3H_5)Co-[P(OR)$_3]_3$.[19] Because of the superficial similarity of (η^3-cyclohexenyl)Co[P(OR)$_3]_2$ and our compound, we attempted the synthesis of (η^5-cyclohexadienyl)Rh[P(O-*i*-$C_3H_7)_3]_2$. Since it has been shown that coordination of arenes to 12-electron IrL_2^+ fragments activates arenes toward nucleophilic attack at an exo position of the aromatic ring,[20] the synthesis of (η^5-cyclohexadienyl)Rh[P(O-*i*-$C_3H_7)_3]_2$ was attempted by the reaction

$$(\eta^6\text{-}C_6H_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2^+ + H^- \rightarrow (\eta^5\text{-cyclohexadienyl})Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$$

This synthetic strategy failed: (η^6-C_6H_6)Rh[P(O-*i*-$C_3H_7)_3]_2{}^+BF_4^-$ reacted with hydride ion in tetrahydrofuran to give {HRh[P(O-*i*-$C_3H_7)_3]_2\}_2$ and C_6H_6. This result could be accounted for by first formation of (η^5-cyclohexadienyl)Rh[P(O-*i*-$C_3H_7)_3]_2$, analogous to the same reaction with iridium,[20] followed by transfer of the endo ring hydrogen to the metal accompanied by ring dissociation to form the arene and the rhodium hydride. Alternatively, the same result could be achieved by direct attack of the hydride ion at the metal center. When the hydride ion was reacted with (η^6-C_6D_6)Rh[P(O-*i*-$C_3H_7)_3]_2{}^+BF_4^-$, {HRh[P-(O-*i*-$C_3H_7)_3]_2\}_2$ was again formed. In this case, gas chromatography–mass spectrometry has shown that the benzene was 6.3% C_6D_5H with the remainder being C_6D_6. Thus, if the exo nucleophilic attack pathway is at all operative in this reaction system, it can account for at most only 6.3% of the reaction. This result is not surprising in view of the fact that we have observed that the arene ligand dissociates significantly in tetrahydrofuran solution (see Experimental Section).[21]

In an attempt to suppress dissociation of the arene and to enhance the stability of an η^5-cyclohexadienyl species, we reacted [η^6-$C_6(CH_3)_6$]Rh[P(O-*i*-$C_3H_7)_3]_2{}^+BF_4^-$ with methyllithium. This reaction, however, gave a high yield of a yellow compound which was not a cyclohexadienyl derivative but rather a complex derived by deprotonation of a methyl group substituent of the aromatic ring. The elemental analysis, mass spectrum, and ^1H NMR spectrum (Table I) suggested that the formula was [C_6-$(CH_3)_5CH_2$]Rh[P(O-*i*-$C_3H_7)_3]_2$ (1), and reaction of hydride ion with [η^6-$C_6(CH_3)_6$]Rh[P(O-*i*-$C_3H_7)_3]_2{}^+$ gave a high yield of the same product. An X-ray crystallographic study confirmed the composition and established a pseudo-square-planar [η^3-$CH_2C_6(CH_3)_5$]Rh[P(O-*i*-$C_3H_7)_3]_2$ structure.

The X-ray structural analysis established that single crystals of (η^3-$CH_2C_6(CH_3)_5$)Rh[P(O-*i*-$C_3H_7)_3]_2$ (1) are composed of discrete mononuclear complexes illustrated in Figure 2. The Rh(I) atom is σ bonded to two phosphite phosphorus atoms and π bonded to the allylic portion of the pentamethylbenzyl ligand. Final atomic coordinates and thermal parameters from the crystallographic study are presented with estimated standard deviations in Tables II and III.[22] Structural parameters for the coordination group of 1 are given in Table IV; ligand bond lengths and angles involving nonhydrogen and hydrogen atoms, respectively, are given in Tables V and VI.[22] The numbering scheme used to designate atoms of 1 is given in ref 23.

Table I. Temperature Dependence of the ABX Pattern Observed in the $^{31}P\{^1H\}$ NMR Spectra for [η^3-$CH_2C_6(CH_3)_5$]Rh[P(O-*i*-$C_3H_7)_3]_2$ [a,b]

temp, °C	chemical shifts, ppm		coupling constants,[c] Hz		
	P_A	P_B	J_{AB}	J_{AX}	J_{BX}
−110	155.33	156.17	82.04	150.21	494.46
−100	154.96	155.82	82.61	159.16	487.91
−90	154.63	155.50	82.78	167.79	480.80
−75	154.61	155.49	83.52	200.20	450.96
−65	154.31	155.20	82.96	213.28	413.19
−45	153.82	154.75	82.48	238.00	416.83
−25	153.31	154.05	82.20	260.87	397.65
−10	153.21	153.72	83.25	261.38	399.79
−5	152.57	153.35	83.00	266.18	395.36
0	152.28	152.56	83.29	261.30	401.61
+10	152.53	152.84	82.85	260.91	403.53
+15	152.51	152.69	82.89	260.72	404.28
+20	152.38	153.37	83.15	350.55	315.25
+35	152.18	153.11	82.95	381.30	286.72
+50	151.79	152.90	82.56	404.40	261.23
+65	151.52	152.82	82.90	411.94	261.20
+80	150.94	152.76	82.12	412.93	261.93

[a] Spectra below −75 °C were recorded in toluene-d_8 / C_5H_{12} (1:3). Other spectra were recorded in toluene-d_8. [b] These temperature dependent spectral changes were fully reversible. [c] Chemical shifts and coupling constants were determined by simulation of the observed spectra.

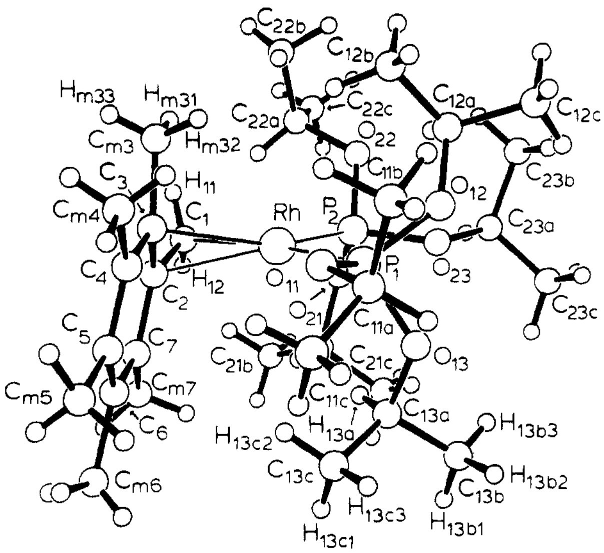

Figure 2. Perspective drawing (adapted from an ORTEP plot) of the (η^3-$CH_2C_6(CH_3)_5$)Rh[P(O-*i*-$C_3H_7)_3]_2$ molecule. For purposes of clarity, rhodium and phosphorus atoms are represented by large open circles, oxygen and carbon atoms by intermediate-sized open circles, and hydrogen atoms by small open circles. The labeling scheme is described in ref 23; labels for many H atoms are omitted in this drawing.

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[19] Bleeke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 556.

[20] Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.*, **1981**, *20*, 2276.

[21] Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 489.

[22] See paragraph at end of paper regarding supplementary material.

Table II. Atomic Coordinates in Crystalline $(\eta^3\text{-CH}_2\text{C}_6(\text{CH}_3)_5)\text{Rh}[\text{P(O-}i\text{-C}_3\text{H}_7)_3]_2$ [a]

atom type[b]	fractional coordinates 10^4x	10^4y	10^4z	atom type[b]	fractional coordinates 10^4x	10^4y	10^4z
Rh	1267.4 (2)	2299.3 (1)	1058.4 (1)	C_{21b}	−847 (4)	3193 (2)	−951 (2)
P_1	3525.5 (7)	2366.6 (3)	1445.6 (3)	C_{21c}	1514 (5)	3744 (2)	−829 (2)
P_2	840.6 (8)	3359.1 (3)	884.9 (4)	C_{22a}	−1661 (3)	3508 (2)	1451 (2)
O_{11}	4115 (2)	1661 (1)	1747 (1)	C_{22b}	−1775 (5)	3269 (3)	2178 (3)
O_{12}	4124 (2)	2876 (1)	2043 (1)	C_{22c}	−2640 (5)	4078 (3)	1278 (3)
O_{13}	4705 (2)	2573 (1)	914 (1)	C_{23a}	2032 (4)	4601 (1)	950 (2)
O_{21}	78 (2)	3587 (1)	150 (1)	C_{23b}	1863 (6)	4886 (2)	1672 (3)
O_{22}	−223 (2)	3741 (1)	1373 (1)	C_{23c}	3346 (6)	4853 (2)	645 (3)
O_{23}	2158 (2)	3866 (1)	984 (1)	C_1	−771 (3)	1966 (1)	685 (2)
C_{11a}	5596 (3)	1544 (2)	1967 (2)	C_2	110 (3)	1370 (1)	684 (1)
C_{11b}	5771 (5)	1566 (3)	2738 (2)	C_3	687 (3)	1129 (1)	1333 (2)
C_{11c}	6015 (4)	880 (2)	1677 (2)	C_4	1679 (4)	585 (2)	1349 (2)
C_{12a}	3265 (3)	3231 (2)	2504 (1)	C_5	2100 (4)	317 (2)	733 (3)
C_{12b}	2648 (5)	2747 (3)	3010 (2)	C_6	1565 (4)	571 (2)	91 (2)
C_{12c}	4245 (5)	3743 (2)	2864 (2)	C_7	600 (4)	1083 (2)	59 (2)
C_{13a}	4446 (3)	2480 (2)	176 (1)	C_{m3}	33 (4)	1316 (2)	2004 (2)
C_{13b}	5316 (5)	3005 (3)	−158 (2)	C_{m4}	2183 (5)	312 (2)	2044 (3)
C_{13c}	4841 (6)	1767 (3)	−11 (2)	C_{m5}	3192 (5)	−256 (2)	747 (4)
C_{21a}	482 (3)	3292 (2)	−497 (2)	C_{m6}	2033 (6)	275 (3)	−590 (3)
				C_{m7}	−34 (6)	1344 (2)	−630 (2)

atom type[b]	fractional coordinates 10^3x	10^3y	10^3z	B, Å^2	atom type[b]	fractional coordinates 10^3x	10^3y	10^3z	B, Å^2
H_{11a}	618 (4)	195 (2)	173 (2)	7 (1)	H_{22b1}	−131 (4)	363 (2)	250 (2)	7 (1)
H_{11b1}	502 (3)	119 (2)	290 (2)	6 (1)	H_{22b2}	−98 (5)	295 (2)	232 (2)	11 (1)
H_{11b2}	542 (6)	202 (3)	297 (3)	15 (2)	H_{22b3}	−267 (5)	318 (2)	228 (2)	11 (1)
H_{11b3}	658 (4)	144 (2)	290 (2)	9 (1)	H_{22c1}	−253 (4)	424 (2)	83 (2)	9 (1)
H_{11c1}	699 (4)	76 (2)	181 (2)	8 (1)	H_{22c2}	−244 (4)	449 (2)	158 (2)	9 (1)
H_{11c2}	542 (4)	56 (2)	183 (2)	7 (1)	H_{22c3}	−357 (5)	398 (2)	129 (2)	11 (1)
H_{11c3}	590 (4)	86 (2)	118 (2)	9 (1)	H_{23a}	117 (3)	471 (2)	65 (2)	6 (1)
H_{12a}	243 (3)	344 (2)	226 (2)	5 (1)	H_{23b1}	181 (4)	542 (2)	164 (2)	8 (1)
H_{12b1}	201 (5)	304 (2)	323 (2)	10 (1)	H_{23b2}	285 (6)	477 (3)	195 (3)	14 (2)
H_{12b2}	196 (6)	246 (3)	272 (3)	13 (2)	H_{23b3}	104 (6)	470 (3)	189 (3)	13 (2)
H_{12b3}	359 (6)	262 (3)	333 (3)	14 (2)	H_{23c1}	355 (4)	465 (2)	19 (2)	8 (1)
H_{12c1}	453 (4)	402 (2)	249 (2)	8 (1)	H_{23c2}	316 (5)	536 (2)	58 (2)	12 (1)
H_{12c2}	497 (5)	348 (2)	318 (2)	10 (1)	H_{23c3}	424 (6)	481 (3)	95 (3)	16 (2)
H_{12c3}	368 (4)	401 (2)	317 (2)	8 (1)	H_{11}	−142 (3)	202 (1)	100 (1)	3 (1)
H_{13a}	349 (3)	255 (1)	6 (1)	4 (1)	H_{12}	−118 (3)	212 (1)	27 (1)	4 (1)
H_{13b1}	515 (4)	301 (2)	−68 (2)	9 (1)	H_{m31}	−64 (4)	166 (2)	197 (2)	7 (1)
H_{13b2}	643 (5)	291 (2)	4 (2)	10 (1)	H_{m32}	82 (4)	147 (2)	234 (2)	9 (1)
H_{13b3}	511 (5)	341 (2)	1 (2)	9 (1)	H_{m33}	−47 (4)	99 (2)	217 (2)	8 (1)
H_{13c1}	471 (5)	175 (2)	−49 (2)	10 (1)	H_{m41}	302 (5)	−3 (3)	205 (3)	12 (2)
H_{13c2}	411 (6)	148 (3)	19 (3)	16 (2)	H_{m42}	152 (5)	5 (2)	222 (2)	11 (1)
H_{13c3}	588 (5)	171 (3)	15 (3)	12 (2)	H_{m43}	244 (5)	64 (2)	234 (2)	10 (1)
H_{21a}	91 (3)	284 (1)	−39 (2)	5 (1)	H_{m51}	289 (5)	−55 (2)	44 (2)	10 (1)
H_{21b1}	−63 (4)	300 (2)	−137 (2)	7 (1)	H_{m52}	304 (6)	−50 (3)	119 (3)	13 (2)
H_{21b2}	−153 (4)	289 (2)	−76 (2)	8 (1)	H_{m53}	413 (7)	−12 (3)	62 (3)	17 (2)
H_{21b3}	−133 (4)	361 (2)	−103 (2)	9 (1)	H_{m61}	287 (4)	32 (2)	−69 (2)	9 (1)
H_{21c1}	228 (4)	376 (2)	−54 (2)	7 (1)	H_{m62}	260 (7)	−21 (3)	−35 (3)	18 (2)
H_{21c2}	178 (4)	357 (2)	−125 (2)	9 (1)	H_{m63}	148 (5)	0 (3)	−79 (3)	12 (2)
H_{21c3}	106 (4)	418 (2)	−92 (2)	9 (1)	H_{m71}	48 (4)	173 (2)	−80 (2)	8 (1)
H_{22a}	−177 (3)	311 (2)	114 (2)	6 (1)	H_{m72}	−11 (4)	101 (2)	−92 (2)	9 (1)
					H_{m73}	−88 (6)	155 (3)	−60 (3)	16 (2)

[a] Numbers in parentheses are the estimated standard deviation of the last significant digit. [b] Atoms labeled in agreement with Figure 3. [c] Isotropic thermal parameter.

The η^3-bonding mode for the allylic grouping is highly unsymmetrical and the Rh···C_{m3} separation (Table IV and Figure 2) is short enough to consider the possibility of multicenter (aliphatic) C–H–Rh bonding. Although such multicenter bonding has been observed or proposed in several molecules[24] having metal-to-aliphatic carbon separations of <3.10 Å, most of these species are quite different from 1. Two of them, $\{(\eta^3\text{-}C_8H_{13})Fe[P(OCH_3)_3]_3{}^+\}$[24a,b] (2) and $(\eta^3\text{-}C_8H_{13})Fe[P(OCH_3)_3]_3$[24a] (3) do, however, provide interesting comparisons with 1. Even though 1 and 2 represent a potentially isoelectronic pair, 1 and 3 have the

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[23] Atoms of the two independent phosphite ligands are distinguished from each other by a first numerical subscript to the appropriate atomic symbol; atoms belonging to different isopropoxy arms of the same ligand are differentiated by a second numerical subscript and carbon atoms within the same isopropyl group by an additional subscripted a, b, or c. Carbon atoms of the allylic group are designated by subscripts 1–3 and those for the remainder of the 6-carbon ring by 4–7. In addition to a subscripted m, each carbon atom of a methyl substituent on the benzyl ligand carries the same numerical subscript as the ring carbon to which it is covalently bonded. Hydrogen atoms carry the same subscripts as the carbon atoms to which they are covalently bonded as well as a final numerical subscript to distinguish (when necessary) between hydrogens bonded to the same carbon.

[24] (a) Williams, J. M.; Brown, R. K.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D. *J. Am. Chem. Soc.* **1978**, *100*, 7407. (b) Brown, R. K.; Williams, J. M.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *ibid.* **1980**, *102*, 981. (c) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *ibid.* **1979**, *101*, 7496. (d) Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *ibid.* **1974**, *96*, 754. (e) Cotton, F. A.; Day, V. W. *J. Chem. Soc., Chem. Commun.* **1974**, 415. (f) Pasquali, M.; Floriana, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1978**, *100*, 4918.

Table IV. Bond Lengths, Polyhedral Edge Lengths, and Bond Angles Subtended at the Rh(I) Atom in the Coordination Group of $[\eta^3\text{-}CH_2C_6(CH_3)_5]Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$[a]

parameter[b]	value	parameter[b]	value
		Distances, Å	
Rh–P_1	2.230 (1)	Rh···C_{m3}	2.958 (4)
Rh–P_2	2.165 (1)		
		Rh···H_{m31}	2.89 (4)
Rh–C_1	2.128 (3)	Rh···H_{m32}	3.02 (4)
Rh–C_2	2.246 (3)		
Rh–C_3	2.453 (3)	P_1···P_2	3.349 (1)
Rh–Cg[c]	2.017	P_1···C_3	3.641 (3)
		P_2···C_1	3.172 (3)
		Angles, Deg	
P_1RhP_2	99.26 (3)	P_1RhC_1	165.3 (1)
		P_2RhC_3	155.8 (1)
P_1RhC_3	101.9 (1)		
P_2RhC_1	95.3 (1)	P_1RhCg[c]	130.3
		P_2RhCg[c]	130.5

[a] The number in parentheses following an entry is the estimated standard deviation of the last significant digit. [b] Atoms are labeled in agreement with Figure 3 and Tables II and III. [c] Cg is the center-of-gravity for the three carbons of the allylic group.

most similar M–C separations, 2.958 (4) and 2.983 (4) Å, respectively, for possible C–H to metal interactions; both are ~0.60 Å longer than the formal three-center–two-electron C–H to metal bond in **2**. These M–C separations would further indicate a stronger C–H to metal interaction in **1** than in **3**, since the M–C distance is 0.025 Å shorter and the metal is ~0.1 Å larger in **1**. However, the unambiguous location and refinement of all hydrogen atom positions in **1** allows us to accurately assess C–H to metal interactions. Clearly such an interaction (even a weak one like that proposed[24c] for **3**) does not exist in **1** because the benzylic methyl group bonded to C_3 is oriented with two of its hydrogen atoms closer to the metal than the third. This conformation would minimize both bonding and steric interactions between the methyl group and the rhodium atom. The magnitude of the carbon–metal separation is alone a valid indicator, respectively, of the presence and the absence of multicenter C–H–M bonding only where the magnitudes are very small and very large.

Thus **1** is simply a conventional 16-electron square-planar d^8 Rh(I) metal complex in which two cis coordination sites are spanned by the η^3-bonded allylic group. An unsymmetrical η^3-bonding pattern is expected for a benzyl anion since most of its negative charge resides on the α-carbon.[25] The observed 0.325-Å elongation of the metal-to-ortho-carbon distance in **1** relative to the metal-to-α-carbon distance is larger than that observed in several other π-benzyl complexes[26] but 0.037 Å smaller than that observed for $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$.[25] The 3-carbon allylic grouping[27a] makes a dihedral angle of 71.5° with the least-squares mean plane of the Rh coordination plane.[27b] Whereas one would normally expect the α- and ortho-carbon atoms of a π-bonded allyl to be on the same side of the coordination plane, carbon atoms C_1 and C_2 are displaced by 0.07 and 0.45 Å, respectively, below the coordination plane[27b] and C_3 is 0.51 Å above it. Presumably, steric repulsions between the rhodium atom and the C_3 methyl substituent are responsible for this slight rotation of the allylic group about the vector from its center of gravity (C_g) to the rhodium atom. The displacements of C_1 (0.15 Å in a direction toward Rh) and C_{m3} (0.31 Å in direction away from Rh) from the 6-carbon benzyl ring mean plane[27c] are consistent with this interpretation; the largest displacement from the ring mean plane for the four remaining methyl carbon atoms is 0.07 Å. Allylic hydrogen atoms H_{11} and H_{12} are "bent back" away from the rhodium atom and are displaced by 0.52 and 0.03 Å, respectively, from the 3-carbon allylic plane.[27a]

The remainder of the coordination group parameters in **1** are unexceptional. The average Rh–P distance of 2.198 (1, 33, 33, 2) Å[28] and the P_1RhP_2 angle of 99.26 (3)° are comparable to the values determined for similar parameters in $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.[6,29] As expected, the long Rh–P bond is trans to the short allylic Rh–C bond. The P_1···P_2 and P_2···C_1 separations are both considerably (>0.4 Å) less than the sum of the appropriate van der Waals radii.[30] The benzylic bond lengths in **1** are quite comparable to those recently reported for $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$[25] and show the same ring C–C bond length alternation. Parameters for the phosphite ligand in **1** are comparable to those observed previously.[6,29,31] The average C–H bond length of 0.97 (4, 6, 22, 57) Å is a typical X-ray value and agrees well with values obtained for similar bonds in other high-precision structural studies.[32] The average bond angle involving a hydrogen atom bonded to an sp^3-hybridized carbon atom in **1** is 109 (3, 5, 32, 120)°.[28] There are no intermolecular contacts in **1** which are substantially less than the van der Waals value.[30]

Consistent with the solid-state structure established through the X-ray crystallographic analysis, $[\eta^3\text{-}CH_2C_6(CH_3)_5]Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ in solution exhibited an ABX-(PP′Rh) ^{31}P NMR spectrum. At no temperature between −110 and +80 °C was there equivalence (NMR time scale) of the two phosphite phosphorus atoms. Accordingly, no fast $\eta^3 \rightleftharpoons \eta^1$ benzylrhodium rearrangement[33,34] can be operative[35] in this complex within this temperature range—

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[25] Bleeke, J. R.; Burch, R. R.; Coulman, C. L.; Schardt, B. C. *Inorg. Chem.* **1981**, *20*, 1316.

[26] (a) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418. (b) Sonada, A.; Bailey, P. M.; Maittis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 346. (c) Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1975**, *96*, 399. (d) *Ibid.* **1975**, *96*, 435.

[27] The least-squares mean planes for the following groups of atoms in **1** are defined by the equation: $aX + bY + cZ = d$, where X, Y, and Z are orthogonal coordinates measures along $\bar{a}$, $\bar{b}$, and $\bar{c}^*$, respectively, of the crystal system: (a) C_1, C_2, and C_3, $a = 0.814$, $b = 0.574$, $c = -0.090$, $d = 1.466$; (b) Rh, P_1, P_2, and C_g (coplanar to within 0.008 Å), $a = -0.343$, $b = 0.081$, $c = 0.936$, $d = 1.895$; (c) C_2, C_3, C_4, C_5, C_6, and C_7 (coplanar to within 0.016 Å), $a = 0.746$, $b = 0.666$, $c = -0.003$, $d = 1.846$.

[28] The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

[29] Brown, R. K.; Williams, J. M.; Fredrich, M. F.; Day, V. W.; Sivak, A. J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2099.

[30] Pauling, L. "The Nature of the Chemical Bond"; 3rd ed., Cornell University Press: Ithaca, NY 1960; p 260.

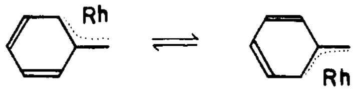
[31] (a) Goh, L.-Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192. (b) Wreford, S. S.; Kouba, J. K.; Kirner, J. F.; Muetterties, E. L.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1558.

[32] (a) Cotton, F. A.; Day, V. W.; Hazen, E. E., Jr.; Larsen, S. *J. Am. Chem. Soc.* **1973**, *95*, 4834. (b) Cotton, F. A.; Day, V. W.; Hazen, E. E., Jr.; Larsen, S.; Wong, S. T. *Ibid.* **1974**, *96*, 4471. (c) Baumgarten, H. E.; McMahan, D. G.; Elia, V. J.; Gold, B. I.; Day, V. W.; Day, R. O. *J. Org. Chem.* **1976**, *41*, 3798. (d) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213. (e) Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2979.

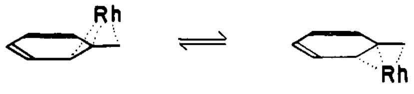
[33] A definitive characterization of an $\eta^3 \rightleftharpoons \eta^1$ rearrangement by NMR studies has not been reported,[34] although they have been "strongly implicated".[34a–d] We note also that no evidence for $\eta^3 \rightleftharpoons \eta^1$ interconversion for benzyl complexes of the cobalt group exists.[34e]

[34] (a) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339. (b) Roberts, J. S.; Klabunde, K. J. *Ibid.* **1977**, *99*, 2509. (c) Becker, Y.; Stille, J. K. *Ibid.* **1978**, *100*, 845. (d) Mann, B. F.; Keasey, A.; Sonada, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 338. (e) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920.

the absence of a fast $\eta^3 \rightleftharpoons \eta^1$ interchange is consistent with the fact that such a process requires a 14-electron intermediate.[35] On the other hand, the two halves of the benzyl ligand which should be inequivalent are not on the NMR time scale in that the two ortho methyl groups on the benzyl ligand are equivalent, as are the two meta methyl groups, over the −75 to +80 °C temperature range. This apparent equivalence would be most readily achieved by a shift of the benzyl ligand as depicted in 4 (a suprafacial shift[34a]).[38] A possible process that would not be sensed in the ^{31}P or ^1H DNMR studies for this specific benzylrhodium complex is a facial shift shown in 5 (an antarafacial shift[34a]).[39] There was a dynamic process operative in this (η^3-benzyl)rhodium species that cannot be explained by any of the foregoing rearrangements. Over the −110 to +80 °C temperature range, the ABX $^{31}P\{^1H\}$ spectrum underwent continuous change in the two ^{31}P chemical shift values and the two ^{31}P–^{103}Rh coupling constants. These changes are tabulated in Table I and are illustrated in Figure 3. The substantial change in the NMR parameters over this temperature range with retention of phosphite phosphorus atom inequivalence requires a rapid (NMR time scale) equilibrium between the ground-state structure in solution, presumably the (η^3-benzyl)rhodium form established for the solid state, and a substantially different excited-state structure with retention of the phosphorus atom inequivalence in the excited-state form and through the interconversion process. We suggest that the excited-state structure is [η^5-$CH_2C_6(CH_3)_5$]Rh[P(O-i-$C_3H_7)_3$]$_2$, a type of benzylmetal complex that has a precedent in organometallic chemistry.[40] The dynamic process, reflected in the temperature-dependent ^{31}P ABX spectra, is as outlined in 6. In principle, phosphorus atom equivalence could be achieved in the η^5 structure by ro-



4



5

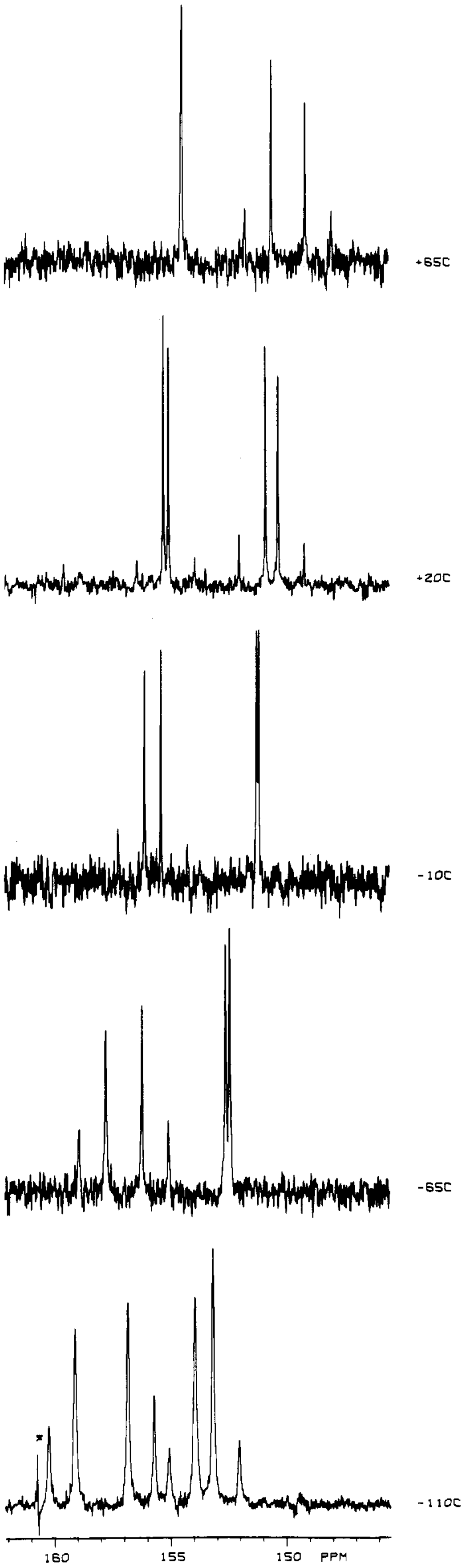


Figure 3. Representation of ^{31}P $\{^1H\}$ NMR spectra of [η^3-$CH_2C_6(CH_3)_5$]Rh[P(O-i-$C_3H_7)_3$]$_2$ demonstrating the temperature dependence of the chemical shifts and rhodium–phosphorus coupling constants. The asterisk in the −110 °C spectrum denotes an electronic artifact.

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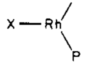
(35) This statement applies only to an η^1-benzylrhodium intermediate of sufficient lifetime that the phosphite phosphorus atoms would be equilibrated. Such a species would be a three-coordinate rhodium complex. Otsuka and co-workers[36] and Van Gaal and Van Den Bekerom[37] have shown for formally analogous $XRh(PR_3)_2$ compounds that there is a bent "T" structure.



If such a geometry prevailed for the putative η^1-benzylrhodium species, equivalence of phosphite phosphorus atoms would be achieved provided that the barrier to rotation about the Rh–C bond is not too high.

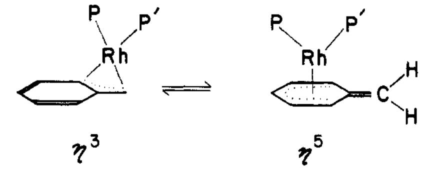
(36) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Chem. Commun.* **1978**, 855.

(37) Van Gaal, H. L. M.; Van Den Bekerom, F. L. A. *J. Organomet. Chem.* **1977**, *134*, 237.

(38) Note that in a permutational context this shift is indistinguishable for the benzylrhodium complex from a rearrangement that proceeds through a η^1 *transition state.*

(39) One plausible geometric pathway for this shift would be through an η^1-benzyl intermediate; however, this geometric pathway does not occur at detectable rates (see Discussion).

(40) Hamon, J. R.; Astruc, D.; Roman, E.; Batail, P.; Mayerle, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 2431.



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tation about the Rh–C_5 centroid vector. No experimental data are available as a guide or measure for such a rotational barrier. However, following the EHMO analysis presented first by Hoffmann and Hofmann[41] for (η^5-benzyl)metal tris(ligand) complexes, we would anticipate a non trivial rotational barrier—one possibly large enough to preclude NMR time scale equilibration of phosphorus atoms in the proposed η^5 excited-state form. In effect, the halfway point in such a rotational process would represent a tetrahedral d^8 rhodium(I) state which should be substantially higher in energy than the square-planar form.[42a] Efforts are currently underway to isolate or spectroscopically detect the excited-state form of the benzylrhodium complex.[42b]

Experimental Section

Reagents and Solvents. All manipulations were carried out under an argon atmosphere in a Vacuum Atmospheres drybox or under a nitrogen atmosphere with use of conventional Schlenk techniques. Toluene, pentane, and tetrahydrofuran solvents were distilled from sodium benzophenone ketyl; 2-propanol was degassed prior to using; and dichloromethane was degassed by three freeze–evacuate–melt cycles and was finally distilled from P_4O_{10}. Toluene-d_8 NMR solvent was purchased from Aldrich or from U.S. Services and was distilled from sodium benzophenone ketyl. Dienes and olefins were purchased from Aldrich or from Chem Samples and were used without further purification. Triisopropropyl phosphite (Aldrich) was degassed by two freeze–evacuate–melt cycles and stirred over sodium sulfate for a minimum of 1 week and was then filtered. Hydrogen was used as received (Matheson). Hexamethylbenzene (Aldrich), potassium triisopropoxyborohydride (1 M in THF) (Aldrich), and methyllithium (low halide, 1.6 M in ether) (Alfa) were used as received.

Spectroscopic and Analytical Methods. Proton NMR spectra were recorded in toluene-d_8 solution at 180 or 250 MHz on instruments using Oxford Superconducting magnets interfaced with Nicolet 1180 computers. Chemical shifts (^1H and ^{13}C) are reported relative to tetramethylsilane. Phosphorus-31 NMR spectra were recorded in toluene-d_8 solution or in toluene-d_8/pentane mixtures at 72.9 MHz on the 180 spectrometer with the chemical shifts reported relative to 85% H_3PO_4. Simulations of spectra were carried out by using the Nicolet Technology Corp.'s program ITRCAL on the Nicolet 1180 computer.

Chromatographic separation of volatile hydrocarbon products were effected with a Perkin-Elmer Sigma 3 instrument (flame ionization detector) and a 12 ft × $^1/_8$ in. 15% dimethylsulfolane on Chromosorb P column. Identification of compounds was confirmed by GC–MS analysis with a Finnegan 4000 instrument interfaced with a Finnegan INCOS data system (30-m SP 2250 (WCOT) column). Mass spectrometric analyses of the rhodium complexes was made with an AEI MS-12 instrument interfaced with an INCOS data system.

Microanalyses were carried out by Mr. Vazken H. Tashinian in the U.C. Berkeley Microanalytical Laboratory.

Preparation of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. To a 100-mL three-neck flask containing a solution of 0.50 g (1.01 mmol) of $[ClRh(C_2H_4)_2]_2$[43] in 30 mL of THF was added 0.85 g (4.09 mmol) of $P(O\text{-}i\text{-}C_3H_7)_3$. Ethylene was evolved immediately. H_2 was then introduced into the flask via a syring needle inlet by piercing a serum cap cover on one of the necks of the flask. A second neck led to an oil bubbler outlet, while the third neck was stoppered. The solution was then cooled to -78 °C, and 2.1 mL of 1 M (2.1 mmol) of $K^+B(O\text{-}i\text{-}C_3H_7)_3H^-$ in tetrahydrofuran was added by syringe. The solution was stirred for 6 h at -78 °C and then at room temperature for an additional 4 h, all under an H_2 atmosphere. The solvent was then removed from the red solution by vacuum distillation. The residue was extracted with pentane (approximately 150 mL), and the green pentane solution was filtered through a fine porosity frit. The solvent volume was reduced by means of vacuum distillation to approximately 40 mL. The solution was cooled to -40 °C to yield large green crystals of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$; yield, 630 mg (60%). This was an improvement of a previously reported synthesis,[3] and the characterization of this compound has been described before.[3]

Preparation of (η^3-Cyclohexenyl)Rh$[P(O\text{-}i\text{-}C_3H_7)_3]_2$. To a solution of 0.20 g (0.19 mmol) of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ in 20 mL of toluene was added approximately 0.5 mL (5.3 mmol) of 1,3-cyclohexadiene. There was a slow color change from dark green to yellow over the course of 3 h. At this point, the solvent and all of the volatile compounds were removed by vacuum distillation. The resulting yellow oil was dissolved in 2-propanol and cooled to -40 °C to precipitate yellow crystals of (cyclohexenyl)Rh$[P(O\text{-}i\text{-}C_3H_7)_3]_2$ which were isolated by filtration and dried under vacuum. Anal. Calcd for $C_{24}H_{51}O_6P_2Rh$: C, 48.00; H, 8.50; P, 10.33. Found: C, 47.60; H, 8.37; P, 10.18; Mass spectrum: 600 amu of parent ion, $P + 1/P = 0.266$ (calcd for 24 carbon atoms: $P + 1/P = 0.276$). ^1H NMR (20 °C) at 250 MHz: +1.25 (overlapping d of d, $J_{H-H} = 6.3$ Hz), +1.55 (m), +2.18 (m), +4.60 (t, $J_{H-H} = 5.6$ Hz), +4.75 (m), +5.05 (t, $J_{H-H} = 6.7$ Hz), +5.75 ppm (m). $^{31}P\{^1H\}$ NMR (+20 °C): +156.9 ppm (d, $J_{Rh-P} = 216.4$ Hz). This spectrum was temperature invariant from -70 to +20 °C.

Reaction of (Cyclohexenyl)Rh$[P(O\text{-}i\text{-}C_3H_7)_3]_2$ with H_2. To a 60-mL reaction tube equipped with a Kontes high vacuum stopcock and a stir bar was added 0.02 g (0.03 mmol) of $(C_6H_9)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ in approximately 5 mL of pentane. The solution was degassed by two freeze–evacuate–melt cycles. Hydrogen gas was then admitted to approximately 1 atm, and the resulting solution was stirred at room temperature. The color changed from yellow to red within ca. 15 min. After 8 h, the volatile compounds were removed by vacuum distillation. Assay of the volatile components showed cyclohexane and cyclohexene in a 1:1 ratio. The metal-containing residues were dissolved in toluene-d_8. The ^1H NMR analysis of the resulting green solution showed that $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ was the major, if not exclusive, metal-containing product. The above procedure was repeated,

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(41) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

(42) (a) We note that no such temperature dependence of ^{31}P NMR chemical shift was reported for the related $(\eta^3\text{-}CH_2C_6H_5)Pd[P(C_2H_5)_3]_2^+$ complex.[34c] (b) We note that the phosphite phosphorus atom, P1, trans to the α-carbon atom of the η^3-$CH_2C_6(CH_3)_5$ ligand, the carbon atom of the allylic set most tightly bound to the rhodium atom, has a significantly longer bond to rhodium than the other phosphite phosphorus atom: 2.230 (1) vs. 2.165 (1) Å. (See Figure 2 and Table IV.) If the magnitude of the Rh–P spin–spin coupling constants is largely determined in this rhodium complex by the Fermi contact contribution, then we would expect the ^{31}P NMR resonance with the smaller spin–spin coupling constant *at low temperatures* would be the one with the longer bond to the rhodium, namely, P1 in the η^3-$CH_2C_6(CH_3)_5$Rh ground-state form (assuming the same structure for the solution state and the crystalline state of the complex). The DNMR ^{31}P spectra show that the smaller J_{PRh} coupling constant increases with temperature increase and the other decreases (the sign of the two coupling constants cannot be established from the spectra but since the coupling constant is based on directly bonded nuclei and since the phosphorus atoms are in relatively similar environments for the square planar η^3-benzyl form, the signs of the two coupling constants are probably identical). If the foregoing premises are correct and if the excited-state form is the above postulated η^5-benzylrhodium species, it follows from 3 that the phosphorus atom (P2) which is trans in the η^5-benzylrhodium form to the para aromatic carbon atom of the benzyl ligand should have the smaller coupling constant for this excited-state form. Consistent with the foregoing arguments, the Rh–P2 (following the labeling in Figure 2 and the rearrangement mechanism outlined in 3) distance in the η^5-benzylrhodium should be the larger of the two Rh–P distances. The P(2) phosphorus atoms in the excited state, η^5-benzylrhodium form would be trans to the para aromatic carbon atom of the η^5-benzyl ligand. The EHMO considerations suggest that this trans phosphite phosphorus atom should have the longer Rh–P distance. (c) We note that an isoelectronic compound (η^3-7-ethylbenzyl)Rh(1,5-cyclooctadiene) has been recently described but no evidence for an excited state structure was reported; cf. Stühler, H. D.; Pickardt, H. *Z. Naturforsch., Anorg. Chem., Org. Chem.* **1981**, *36B*, 315. The crystallographic study showed this η^3-benzyl ligand to have a more symmetric bonding to the rhodium atom than observed in our complex.

(43) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

Table V. Bond Lengths and Angles Involving Nonhydrogen Ligand Atoms in Crystalline $[\eta^3\text{-}CH_2C_6(CH_3)_5]Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ [a]

parameter [b]	value	parameter [b]	value
		Bond Lengths, Å	
$\mathrm{P_1-O_{11}}$	1.605 (2)	$\mathrm{C_{11a}-C_{11b}}$	1.486 (6)
$\mathrm{P_1-O_{12}}$	1.611 (2)	$\mathrm{C_{11a}-C_{11c}}$	1.495 (5)
$\mathrm{P_1-O_{13}}$	1.611 (2)	$\mathrm{C_{12a}-C_{12b}}$	1.512 (6)
$\mathrm{P_2-O_{21}}$	1.617 (2)	$\mathrm{C_{12a}-C_{12c}}$	1.518 (5)
$\mathrm{P_2-O_{22}}$	1.608 (2)	$\mathrm{C_{13a}-C_{13b}}$	1.498 (6)
$\mathrm{P_2-O_{23}}$	1.607 (2)	$\mathrm{C_{13a}-C_{13c}}$	1.513 (6)
av [c]	1.610 (2, 3, 7, 6)	$\mathrm{C_{21a}-C_{21b}}$	1.505 (5)
		$\mathrm{C_{21a}-C_{21c}}$	1.498 (6)
$\mathrm{O_{11}-C_{11a}}$	1.462 (4)	$\mathrm{C_{22a}-C_{22b}}$	1.489 (6)
$\mathrm{O_{12}-C_{12a}}$	1.425 (4)	$\mathrm{C_{22a}-C_{22c}}$	1.488 (6)
$\mathrm{O_{13}-C_{13a}}$	1.442 (3)	$\mathrm{C_{23a}-C_{23b}}$	1.519 (6)
$\mathrm{O_{21}-C_{21a}}$	1.449 (4)	$\mathrm{C_{23a}-C_{23c}}$	1.494 (7)
$\mathrm{O_{22}-C_{22a}}$	1.454 (4)	av [c]	1.501 (6, 10, 18, 12)
$\mathrm{O_{23}-C_{23a}}$	1.466 (4)		
av [c]	1.450 (4, 11, 25, 6)	$\mathrm{C_2-C_7}$	1.434 (4)
		$\mathrm{C_3-C_4}$	1.431 (4)
$\mathrm{C_1-C_2}$	1.449 (4)	av [c]	1.433 (4, 2, 2, 2)
$\mathrm{C_2-C_3}$	1.420 (4)		
av [c]	1.435 (4, 15, 15, 2)	$\mathrm{C_3-C_{m3}}$	1.512 (5)
		$\mathrm{C_4-C_{m4}}$	1.497 (7)
$\mathrm{C_4-C_5}$	1.380 (6)	$\mathrm{C_5-C_{m5}}$	1.537 (6)
$\mathrm{C_5-C_6}$	1.404 (6)	$\mathrm{C_6-C_{m6}}$	1.526 (7)
$\mathrm{C_6-C_7}$	1.366 (5)	$\mathrm{C_7-C_{m7}}$	1.517 (5)
av [c]	1.383 (6, 14, 21, 3)	av [c]	1.518 (6, 11, 21, 5)
		Bond Angles, Deg	
$\mathrm{RhP_1O_{11}}$	112.1 (1)	$\mathrm{RhC_1C_2}$	75.1 (2)
$\mathrm{RhP_1O_{12}}$	124.7 (1)	$\mathrm{RhC_2C_3}$	80.6 (2)
$\mathrm{RhP_1O_{13}}$	119.3 (1)	$\mathrm{RhC_3C_2}$	64.6 (2)
$\mathrm{RhP_2O_{21}}$	118.5 (1)	$\mathrm{RhC_2C_1}$	66.3 (2)
$\mathrm{RhP_2O_{22}}$	119.1 (1)	$\mathrm{RhC_2C_7}$	14.9 (2)
$\mathrm{RhP_2O_{23}}$	117.0 (1)	$\mathrm{RhC_3C_4}$	24.3 (2)
av [c]		$\mathrm{RhC_3C_{m3}}$	93.4 (2)
		$\mathrm{C_1C_2C_3}$	117.9 (2)
$\mathrm{O_{11}P_1O_{12}}$	100.9 (1)	$\mathrm{C_7C_2C_3}$	118.7 (3)
$\mathrm{O_{11}P_1O_{13}}$	102.3 (1)	$\mathrm{C_2C_3C_4}$	119.5 (3)
$\mathrm{O_{12}P_1O_{13}}$	93.8 (1)	$\mathrm{C_3C_4C_5}$	119.6 (3)
$\mathrm{O_{21}P_2O_{22}}$	96.7 (1)	$\mathrm{C_4C_5C_6}$	120.8 (4)
$\mathrm{O_{21}P_2O_{23}}$	103.6 (1)	$\mathrm{C_5C_6C_7}$	121.0 (3)
$\mathrm{O_{22}P_2O_{23}}$	98.3 (1)	$\mathrm{C_6C_7C_2}$	120.3 (3)
av [c]	99.3 (1, 30, 55, 6)	$\mathrm{C_7C_2C_1}$	122.6 (3)
		$\mathrm{C_2C_3C_{m3}}$	121.0 (3)
$\mathrm{P_1O_{11}C_{11a}}$	123.5 (2)	$\mathrm{C_4C_3C_{m3}}$	118.0 (3)
$\mathrm{P_1O_{12}C_{12a}}$	124.4 (2)	$\mathrm{C_3C_4C_{m4}}$	117.9 (3)
$\mathrm{P_1O_{13}C_{13a}}$	120.6 (2)	$\mathrm{C_5C_4C_{m4}}$	122.5 (4)
$\mathrm{P_2O_{21}C_{21a}}$	120.9 (2)	$\mathrm{C_4C_5C_{m5}}$	119.8 (4)
$\mathrm{P_2O_{22}C_{22a}}$	122.2 (2)	$\mathrm{C_6C_5C_{m5}}$	119.4 (4)
$\mathrm{P_2O_{23}C_{23a}}$	123.9 (2)	$\mathrm{C_5C_6C_{m6}}$	120.8 (4)
av [c]	122.6 (2, 13, 20, 6)	$\mathrm{C_7C_6C_{m6}}$	118.3 (4)
		$\mathrm{C_6C_7C_{m7}}$	121.7 (3)
$\mathrm{O_{11}C_{11a}C_{11b}}$	109.7 (3)	$\mathrm{C_2C_7C_{m7}}$	118.0 (3)
$\mathrm{O_{11}C_{11a}C_{11c}}$	107.5 (3)		
$\mathrm{O_{12}C_{12a}C_{12b}}$	110.0 (3)	av [c]	120.0 (3, 13, 26, 17)
$\mathrm{O_{12}C_{12a}C_{12c}}$	105.1 (3)	$\mathrm{C_{11b}C_{11a}C_{11c}}$	112.6 (3)
$\mathrm{O_{13}C_{13a}C_{13b}}$	105.5 (3)	$\mathrm{C_{12b}C_{12a}C_{12c}}$	112.3 (3)
$\mathrm{O_{13}C_{13a}C_{13c}}$	109.0 (3)	$\mathrm{C_{13b}C_{13a}C_{13c}}$	113.5 (3)
$\mathrm{O_{21}C_{21a}C_{21b}}$	107.4 (3)	$\mathrm{C_{21b}C_{21a}C_{21c}}$	112.0 (3)
$\mathrm{O_{21}C_{21a}C_{21c}}$	109.6 (3)	$\mathrm{C_{22b}C_{22a}C_{22c}}$	120.0 (3)
$\mathrm{O_{22}C_{22a}C_{22b}}$	108.4 (3)	$\mathrm{C_{23b}C_{23a}C_{23c}}$	111.7 (3)
$\mathrm{O_{22}C_{22a}C_{22c}}$	108.2 (3)		
$\mathrm{O_{23}C_{23a}C_{23b}}$	110.1 (3)	av [c]	112.3 (3, 5, 12, 6)
$\mathrm{O_{23}C_{23a}C_{23c}}$	106.4 (3)		
av [c]	108.1 (3, 14, 30, 12)		

[a] The number in parentheses following an individual entry is the estimated standard deviation for the last significant digit. [b] Atoms labeled in agreement with Figure 3 and Tables II and III. [c] See ref 28.

using toluene instead of pentane. The color changed from yellow to brown within ~15 min. After the solution was stirred at room temperature for ~24 h, the volatile components were removed by vacuum distillation. Gas chromatographic analysis of the volatile components revealed the presence of cyclohexane, cyclohexene, and methylcyclohexane in a ratio of 10:1:3. The metal-containing residues were dissolved in toluene-d_8. The NMR analysis of the resulting brown solution showed three sets of complex resonances at +5.2, +4.8, and +4.2 ppm as well as other sharp resonances in the region +1.0 to +1.5 ppm, indicating that there were three triisoproptopyl phosphite environments. Other resonances of low intensity were observed in the region +1.7 to +2.4 ppm and +3.4 to +3.6 ppm. No resonances for metal hydrides could be detected. Since there was a possibility that the

Rh(phosphite)$_2$ fragments still had an aromatic molecule (or fragment) in the coordination sphere, the toluene-d_8 was removed by vacuum distillation, and the residue was dissolved in pentane and degassed. Hydrogen was then admitted to the reaction tube to a pressure of 0.7 atm, and the solution was stirred at room temperature for approximately 8 h. The pentane was removed by vacuum distillation, and the residue was dissolved in toluene-d_8. The brown color persisted, and the NMR spectrum showed no spectral changes.

Dehydrogenation of 1,3-C_6H_8 Using $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. To a solution of 0.020 g (0.019 mmol) of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ in 1.50 mL of toluene contained in reaction tube of 50-mL volume was added 60.0 μL (0.89 mmol) of 1,3-C_6H_8. The solution was then degassed by two freeze–evacuate–melt cycles. The solution was allowed to warm to room temperature and to stir for 12 h. Quantitative assay by gas chromatography using standard solutions showed that 1.2 equiv of C_6H_6 was produced per 1 equiv of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. This reaction was repeated with 0.020 g (0.019 mmol) of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, 0.10 mL (1.49 mmol) of 1,3-C_6H_8, and 1.50 mL of toluene for 24 h. The gas chromatography assay revealed that 1.02 equiv of C_6H_6 was generated per 1 equiv of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. This reaction was repeated in pentane solution; the yield of benzene was the same.

The yield of C_6H_6 was enhanced by the addition of 1-hexene: the above reaction was repeated with 0.020 g (0.019 mmol) of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, 0.10 mL (1.49 mmol) of 1,3-C_6H_8, 0.10 mL (1.77 mmol) of 1-hexene, and 1.50 mL of toluene for 24 h. The gas chromatography assay revealed that 1.84 equiv of C_6H_6 was generated per 1 equiv of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.

NMR monitoring of the reaction of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ with 1,3-C_6H_8 showed that the resonances for $(C_6H_9)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ and C_6H_6 uniformly increased and that no intermediates were detectable.

Reaction of $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ with 1,3-C_6H_8. A solution of 0.020 g (0.019 mmol) of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ and 0.10 mL (1.49 mmol) of 1,3-cyclohexadiene in approximately 2 mL of toluene was placed in a reaction tube of 75-mL volume. The resulting solution was degassed by two freeze–evacuate–melt cycles. Hydrogen was then introduced to a pressure of ca. 0.5 atm. As the solution thawed, the red color for $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ quickly appeared. When the color change was complete, the solution was again frozen, and the excess hydrogen was removed by evacuation. The reaction tube was isolated from the vacuum line, and the solution was allowed to warm to room temperature. The color of the solution then changed over the course of ca. 15 min from red for the tetrahydride to green for $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. However, it is unlikely that $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ was the major species in solution at that point; the intense green color of that compound masked that of the red $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ or the yellow (η^3-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$. The color of the solution gradually turned yellow within ca. 3 h, characteristic of the cyclohexenyl compound. The volatile components were removed by vacuum distillation after a 15-h period and were assayed by gas chromatography. No cyclohexene or cyclohexane could be detected.

Preparation of $(C_6H_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$. This compound was prepared by a modification of literature procedures for other (arene)Rh[phosphine]$_2{}^+$ compounds.[44,45] To a solution of 0.20 g (0.51 mmol) of $[ClRh(C_2H_4)_2]_2$[43] in approximately 30 mL of tetrahydrofuran was added 0.43 g (2.06 mmol) of $P(O\text{-}i\text{-}C_3H_7)_3$. The solution was stirred at room temperature for an additional hour. Tetrahydrofuran was then removed by vacuum distillation. To the solid residue was added 0.20 g (1.03 mmol) of $AgBF_4$ and approximately 0.5 mL (ca. 5.6 mmol) of C_6H_6 in 50 mL of CH_2Cl_2. The resulting solution was stirred at room temperature for 12 h, at which time the CH_2Cl_2 was removed by vacuum distillation. The residue was extracted with approximately 50 mL of tetrahydrofuran and filtered through a fine porosity frit. The solvent volume was reduced by means of vacuum distillation to approximately 25 mL, and pentane (~15 mL) was then added. The solution was cooled to −40 °C. After 12 h, a crop of yellow crystals was isolated by filtration; yield, 510 mg (73%). Anal. Calcd for $C_{24}H_{48}BF_4O_6P_2Rh$: C, 42.12; H, 7.02. Found: C, 41.66, 41.60; H, 7.03, 7.04. Proton NMR (35 °C) at 90 MHz in tetrahydrofuran showed two resonances in the aromatic region at +7.24 ppm for free C_6H_6 and +6.84 ppm for coordinated C_6H_6 in a ratio of 3.5:1.

The $C_6D_6Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$ compound was similarly prepared. Anal. Calcd for $C_{24}H_{42}D_6BF_4O_6P_2Rh$: C, 41.75; H, 6.92. Found: C, 40.72; H, 6.79 (the hydrogen analysis was effected by measuring the weight of water after combustion).

Reaction of $(C_6H_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$ with $K^+B(O\text{-}i\text{-}C_3H_7)_3H^-$. A solution of 0.25 g (0.37 mmol) of $(C_6H_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$ dissolved in 40 mL of tetrahydrofuran with 5 mL of C_6H_6 in a Schlenk flask was cooled to −78 °C. The solution at this point was pale yellow. To the solution was added 0.40 mL of 1 M solution of $K^+B(O\text{-}i\text{-}C_3H_7)_3H^-$ (0.40 mmol) in tetrahydrofuran. The pale yellow solution became a deep yellow color within approximately 10 min. The solution was stirred at −78 °C for an additional 90 min, at which time the solution was allowed to warm to room temperature. The solution was then stirred for an additional hour during which the solution became dark green. The solvent was then removed by vacuum distillation. The residues were extracted with pentane and filtered through a fine porosity frit; pentane was removed by vacuum distillation. The green residue was dissolved in toluene-d_8, and the NMR analysis showed that the major product was $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.

The above reaction was repeated by using $(C_6D_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$ with no added C_6H_6 or C_6D_6. Following the low-temperature addition of $K^+B(O\text{-}i\text{-}C_3H_7)_3H^-$ and allowing the solution to warm to room temperature for 1 h, the volatile components were isolated by vacuum distillation. Assay of the volatile components showed C_6D_6 and C_6D_5H in a ratio of 1.0:0.063. The ^1H NMR analysis of the metal-containing portion revealed the presence of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$.

Preparation of $[\eta^3\text{-}CH_2C_6(CH_3)_5]Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$. To a solution of 0.135 g (0.180 mmol) of $(C_6(CH_3)_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$ in 50 mL of tetrahydrofuran which was cooled to −78 °C was added 0.125 mL (0.20 mmol) of 1.6 M CH_3Li (low halide) in ether. The solution was allowed to warm to room temperature and was stirred for an additional 1 h. The solvent was removed from the deep yellow solution by vacuum distillation. The residue was extracted with pentane and filtered through a fine porosity frit. The solvent volume was reduced to the minimum possible without inducing cloudiness and was then cooled to −40 °C for 24 h. A crop of yellow crystals was isolated by filtration which were dried under vacuum; yield, 80 mg (65%). Anal. Calcd for $C_{30}H_{59}O_6P_2Rh$: C, 52.94; H, 8.68; P, 9.12. (The sample used for the analysis was crystallized from 2-propanol.) Found: C, 52.50; H, 8.61; P, 8.04. Mass spectrum: 680 amu of parent ion, $P + 1/P = 0.374$ (calcd for 30 carbon atoms: $P + 1/P = 0.33$). Proton NMR (20 °C) at 250 MHz in toluene-d_8: +4.95 (m, 3 H), +4.59 (m, 3 H), +2.32 (d, 2 H, $J_{Rh-H} = 8.8$ Hz), +2.25 (s, 6 H), +2.14 (m, 3 H), +2.03 (s, 3 H), +1.35 (d, 18 H, $J_{H-H} = 3.0$ Hz), +1.20 ppm (d, 18 H, $J_{H-H} = 2.5$ Hz). Both the ^1H and $^{31}P\{^1H\}$ (an ABX spectrum) are temperature dependent (see Discussion).

The above reaction was repeated by using $K^+B(O\text{-}i\text{-}C_3H_7)_3H^-$ instead of CH_3Li. The result was the same: $[(CH_2C_6(CH_3)_5]Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ was isolated from the reaction.

X-ray Crystallographic Study[22] of $(\eta^3\text{-}CH_2C_6(CH_3)_5)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ (1). Large, well-shaped yellow crystals of $(\eta^3\text{-}CH_2C_6(CH_3)_5)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ (1) were obtained by cooling a pentane solution to −40 °C. They are, at 20 ± 1 °C, monoclinic with $a = 9.478$ (3) Å, $b = 19.857$ (8) Å, $c = 19.275$ (8) Å, $\beta = 93.25$ (3)°, $V = 3621.8$ Å^3, and $Z = 4$ (μ_a(Mo $K\bar{\alpha}$)[46a] = 0.58 mm^{-1}; $d_{calcd} = 1.25$ g cm^{-3}). The systematically absent reflections in the diffraction pattern were those for the uniquely determined centrosymmetric space group $P2_1/c$—C_{2h}^5 (No. 14).[47]

Intensity measurements were made on a Nicolet $P\bar{1}$ autodiffractometer using 1.1° wide ω scans and graphite-monochromated Mo $K\bar{\alpha}$ radiation for a specimen having the shape of a rectangular parallelepiped with dimensions of 0.44 × 0.44 × 0.75 mm. This

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(44) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

(45) Uson, R.; Lahuerta, P.; Reyes, J.; Oro, L. A.; Foces-Foces, C.; Cane, F. H.; Garcia-Blanco, S. *Inorg. Chim. Acta* **1980**, *42*, 75.

(46) (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55–66. (b) *Ibid.*, pp 99–101. (c) *Ibid.*, pp 149–150.

(47) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. 1, p 99.

crystal was mounted on the goniometer head with its long dimension nearly parallel to the phi axis of the diffractometer. A total of 8327 independent reflections having $2\theta_{MoK\bar{\alpha}} < 55°$ (the equivalent of 1.0 limiting Cu $K\bar{\alpha}$ spheres) were measured in two concentric shells of increasing 2θ, each of which contained approximately 4150 reflections. A scanning rate of 6°/min was used for all others. Each of these 1.1° wide scans were divided into 19 equal (time) intervals, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth the total time used for the net scan (13/19 of the total scan time), were measured at ω settings 1.1° above and below the calculated $K\bar{\alpha}$ doublet value for each reflection. Since ψ scans for several intense reflections confirmed the anticipated absence of variable absorption for this sample, the intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of appropriate Lorentz and polarization corrections.

The structure was solved by using the "heavy-atom" technique. Unit-weighted full-matrix least-squares refinement which utilized anisotropic thermal parameters for all 39 crystallographically independent nonhydrogen atoms converged to R_1 (unweighted, based on F)[48] = 0.046 and R_2 (weighted, based on F)[48] = 0.057 for 3482 independent reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. A difference Fourier synthesis at this point permitted the location of all 59 hydrogen atoms in the asymmetric unit. All additional least-squares cycles for 1 refined hydrogen atoms with isotropic thermal parameters and nonhydrogen atoms with anisotropic thermal parameters. Unit-weighted cycles gave $R_1 = 0.023$ and $R_2 = 0.025$ with 3482 reflections. Similar unit-weighted refinement cycles with the more complete ($2\theta_{MoK\bar{\alpha}} < 55°$) data set gave $R_1 = 0.028$ and $R_2 = 0.029$ for 6133 reflections. The final cycles of empirically weighted[49] full-matrix least-squares refinement with 98 independent atoms gave $R_1 = 0.028$ and $R_2 = 0.034$ for 6133 independent reflections having $2\theta_{MoK\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$. Since a careful comparison of final F_o and F_c values[22] indicated the absence of extinction effects, extinction corrections were not made.

All structure factor calculations employed recent tabulations of atomic form factors[46b] and anomalous dispersion corrections[46c] to the scattering factors of the Rh and P atoms. All calculations were performed on a Data General Eclipse S-200 computer with 65K of 16-bit words, a floating point processor for 32- and 64-bit arithmetic and versions of the Nicolet E-XTL interactive crystallographic software package as modified at Crystalytics Co.

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Registry No. 1, 79499-71-1; $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, 70727-44-5; ($\eta^3$-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$, 79499-72-2; $(C_6H_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$, 79499-74-4; $(C_6(CH_3)_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$, 79499-76-6; $[ClRh(C_2H_4)_2]_2$, 12081-16-2; 1,3-C_6H_8, 592-57-4; C_6H_6, 71-43-2.

Supplementary Material Available: Crystal structure analysis report, anisotropic thermal parameters (Table III), bond lengths and angles involving hydrogen atoms (Table VI), and a listing of structure factors for $(\eta^3\text{-}CH_2C_6(CH_3)_5)Rh[P\text{-}(O\text{-}i\text{-}C_3H_7)_3]_2$ (38 pages). Ordering information is given on any current masthead page.

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(48) The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

(49) Empirical weights were calculated from the equation $\sigma = \sum_0^2 a_n|F_o|^n = 0.769 + (3.00 \times 10^{-3})F_o + (1.09 \times 10^{-5})|F_o|^2$, the a_n being coefficients derived from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^2 a_n|F_o|^n$, where F_c values were calculated from the fully refined model using unit weighting and an $I > 3\sigma(I)$ rejection criterion.

Hydrido Formyl, Methoxycarbonyl, Hydroxymethyl, and Methyl Complexes of Iridium: Syntheses and Reactivities[†]

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Several hydrido formyl complexes of iridium(III) have been isolated and their chemical properties examined. Two synthetic methods have been employed. The oxidative addition of a C–H bond of formaldehyde to reactive Ir(I) compounds has been used for the preparation of $[IrH(CHO)(P(CH_3)_3)_4][PF_6]$ (3), $IrClH(CHO)(P(CH_3)_3)_3$ (4), and $Ir(CH_3)H(CHO)(P(CH_3)_3)_3$ (5). The reduction of (methoxycarbonyl)iridium(III) compounds $[IrH(CO_2CH_3)(P(CH_3)_3)_4][PF_6]$ (1) and $IrClH(CO_2CH_3)(P(CH_3)_3)_3$ (2), prepared respectively by addition of methanol to $[Ir(CO)(P(CH_3)_3)_4]^+$ and oxidative addition of methyl formate by $IrCl(C_8H_{14})(P(CH_3)_3)_3$, has also been used for the preparation of the formyl compounds 3 and 4. Reduction of the formyl group of 3 to hydroxymethyl and to methyl groups has been demonstrated; thus, the reduction of carbon monoxide to a methyl group has been achieved and the intermediate complexes, containing formyl and hydroxymethyl groups, have been characterized. This conversion takes place even in the presence of a hydrido ligand. Facile reductive elimination, which might be expected for compounds containing a hydrido ligand cis to a carbon-bound organic fragment, is not observed.

Introduction

Intense interest in the transition-metal-mediated reactions of carbon monoxide with hydrogen to form utilizable organic products[1] has prompted many investigations of compounds which serve as models for postulated intermediates in carbon-monoxide hydrogenation.[2] These in-

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[†] Contribution No. 2937.

(1) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172.