1260 *Organometallics* **1987**, *6*, 1260–1267

The Chemistry of Bulky Chelating Phosphines. 3. Anionic Alkyl and Aryl Complexes of Rhodium(I) and Iridium(I)

Alan A. Del Paggio,*[†] Richard A. Andersen, and Earl L. Muetterties[‡]

Department of Chemistry, University of California, Berkeley, California 94720

Received August 28, 1986

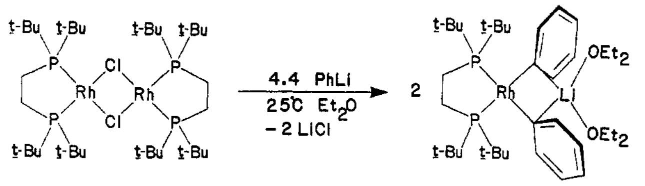
A series of thermally stable anionic dialkyl-, diaryl-, and dialkynylrhodium(I) and dialkyl-, diaryl-, and dialkynyliridium(I) bis(phosphine) complexes of the general formula (dtbpe)$MR_2Li(OR'_2)_x$ (M = Rh, Ir; dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) have been prepared and characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The anionic complexes are monomeric in polar and nonpolar solvents as determined by multinuclear NMR spectroscopy. Crossover experiments indicate that the complexes (dtbpe)$MR_2Li(OR'_2)_x$ are inert with respect to exchange of their hydrocarbon ligands in solution. Protonation of (dtbpe)$MR_2Li(OR'_2)_x$ affords either $\{(\mu\text{-OH})Ir(dtbpe)\}_2$ (H_2O) or $\{(\mu\text{-H})Rh(dtbpe)\}_2$ (*i*-PrOH). The latter reaction apparently proceeds via a series of protonation/reductive elimination sequences followed ultimately by a β-hydride abstraction from the coordinated alkoxide ligand. The (dtbpe)$MR_2Li(OR'_2)_x$ complexes also act as mild alkylating agents toward transition-metal halide complexes.

Introduction

Anionic transition-metal complexes have received considerable attention due to their reactivity toward organic molecules[1] as well as their utility for the preparation of homo- and heteronuclear transition-metal clusters.[2] Anionic complexes are usually stabilized by π-acid ligands such as carbonyl[3] and olefin[4] although anionic transition-metal complexes containing PF_3,[5] $P(OR)_3$,[6] and PMe_3[7] are also known. Recent work in our laboratories has led to the characterization of a series of anionic rhodium(I) and iridium(I) olefin alkyl complexes of the type $[(\eta^4\text{-}1,5\text{-}COD)MR_2][Li]$ and $[(\eta^4\text{-}1,5\text{-}COD)MR_2][Li(tmeda)]$ (M = Rh, Ir; R = Me, CH_2SiMe_3).[8] We sought to extend this family of compounds by replacing the olefin ligands in $[(\eta^4\text{-}1,5\text{-}COD)MR_2][Li(tmeda)]$ with phosphines.[9] Since phosphines are better σ-donors and weaker π-acceptors than olefins, it is reasonable to expect the increased charge density to localize at the metal center, thereby enhancing its reactivity toward electrophilic reagents.[10,11]

Results and Discussion

Late-transition-metal alkyl anions have been prepared by a variety of routes, the most common of which involves displacement of neutral ligands such as thioether, olefin-,[4,12b] tertiary amine,[12a] or phosphine[12c,d] by an organolithium reagent. While organolithium reagents do not displace PMe_3 from the neutral complexes $RM(PMe_3)$(dtbpe) or $RM(PMe_3)$(dippe) (M = Rh, Ir; R = Me, C_6H_5; dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane; dippe = 1,2-bis(diisopropylphosphino)ethane), the desired dialkyl-, diaryl-, and dialkynyl anions can be prepared directly from $\{(\mu\text{-Cl})Rh(dtbpe)\}_2$[13,14a] (**1**), $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$,[13,14a] (**2**) or $\{(\mu\text{-Cl})Rh(dippe)\}_2$[13] (**3**) and 4 molar equiv of the appropriate organolithium reagent (eq 1). Rates of alkylation are generally higher for **1** than for **2**, consistent with the observed reluctance of **2** toward ionization of its halide lig-



(1)

[†] To whom correspondence should be addressed at Shell Development Company, Westhollow Research Center, P.O. Box 1380, Houston, TX 77001.

[‡] Deceased January 12, 1984.

(1) (a) King, R. B. *Adv. Organomet. Chem.* **1964**, *2*, 157. (b) *Organometallic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Interscience: New York, 1968. (c) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489. (d) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 219. (e) Krause, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2972.

(2) (a) Anders, U.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1966**, 291. (b) Tachikawa, M.; Sievert, A. C.; Muetterties, E. L.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1725. (c) Tachikawa, M.; Muetterties, E. L.; Geerts, R. L. *J. Organomet. Chem.* **1981**, *213*, 11.

(3) (a) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (b) Ellis, J. E.; Faltynek, R. A.; Hentges, S. G. *J. Organomet. Chem.* **1976**, *120*, 389. (c) Ellis, J. E.; Faltynek, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 1801. (d) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, *19*, 686. (e) Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357. (f) Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 3605.

(4) (a) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 997. (b) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 752. (c) Jonas, K.; Mynott, R.; Krüger, C.; Sekutowski, J. C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 767. (d) Jonas, K.; Porschke, K. R.; Krüger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 621. (e) Bonnemann, H.; Krüger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 46. (f) Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 48. (g) Brauer, D. J.; Krüger, C.; Sekutowski, J. C. *J. Organomet. Chem.* **1979**, *178*, 249. (h) Jonas, K.; Schieferstein, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 549. (i) Jonas, K.; Schieferstein, L.; Krüger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 550. (j) Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520. (k) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295. (l) Jonas, K. *Adv. Organomet. Chem.* **1900**, *19*, 97. Sodium interactions are similar: (m) Müller, E.; Krause, J.; Schmiedeknecht, K. *J. Organomet. Chem.* **1972**, *127*, 44. (n) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434.

(5) Bennett, M. A.; Patmore, J. D. *Inorg. Chem.* **1971**, *10*, 2387.

(6) (a) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920. (b) Watson, P. L.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978.

(7) (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944. (b) Klein, H. F.; Schmidbaur, H.; Karsch, H. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637. (c) Hammer, R.; Klein, H. F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 138. (d) Klein, H. F.; Schmidbaur, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 762. (e) Klein, H. F.; Wenninger, J.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1391.

(8) Kulzick, M. A. Ph.D. Thesis, University of California, Berkeley, 1984.

(9) Reaction of the anionic complex $(\eta^4\text{-}1,5\text{-}COD)IrMe_2Li(OEt_2)_x$ with 1 molar equiv of a bidentate phosphine PP (PP = $R_2PCH_2CH_2PR_2$; R = Me, Et, *i*-Pr) yields the fluxional complexes $MeIr(PP)(\eta^4\text{-}1,5\text{-}COD)$ and methyllithium. No reaction occurs between the COD dimethyliridate and dtbpe (PP with R = *t*-Bu). Del Paggio, A. A.; Andersen, R. A., unpublished results.

0276-7333/87/2306-1260$01.50/0 © 1987 American Chemical Society

ands.[15] Because of this, the conditions required to alkylate **2** are more severe than those required to alkylate **1** or **3** and the isolated yields of the iridates are lower than those of their rhodium analogues.[16]

The bulky chelating phosphine 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe) used in this study is advantageous for a variety of reasons. Since dtbpe is bidentate, it should not be easily displaced from the metal center. The cis phosphine geometry imposed by the bidentate ligand requires the trans-labilizing alkyl, aryl, and alkynyl ligands to be trans to phosphorus. Once formed the anions are kinetically stabilized by the bulky phosphine that retards the rates of associative reactions.[13,14a] Isolation of $(dtbpe)MR_2Li(OEt_2)_x$ is also facilitated by dtbpe since its complexes tend to be relatively insoluble in saturated hydrocarbons at low temperature. Determination of the stereochemistry at the metal centers is straightforward; the *tert*-butyl groups serve as convenient stereochemical probes, as outlined previously.[13,14a]

The C_{2v} symmetry expected for the square-planar $[(dtbpe)MR_2]^-$ anion is fully supported by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy (see Tables I–V). In the ^1H NMR spectra of $(dtbpe)MR_2Li(OR'_2)_x$ the 12 dtbpe methyl groups appear as a single virtual triplet as do the four dtbpe methylene protons. In several complexes the dtbpe methylene proton resonances occurred at the same chemical shift as the dtbpe methyl protons. Ether content in $(dtbpe)MR_2Li(OR'_2)_x$ was variable, depending upon M and R, and was determined for each molecule by integration of its ^1H NMR spectrum relative to the 36 dtbpe methyl protons. Inspection of the $^{31}P\{^1H\}$ NMR spectra of $(dtbpe)MR_2Li(OR'_2)_x$ revealed that both the chemical shifts, δ, and phosphorus–rhodium coupling constants, $^1J_{PRh}$ (^{103}Rh; $I = {}^1/_2$, 100% abundance), are comparable to those observed for the dtbpe phosphorus nucleus trans to the alkyl or aryl ligands in the neutral complexes $RM(PMe_3)(dtbpe)$ (M = Rh, Ir).[13] Only in the $^{13}C\{^1H\}$ NMR spectra of $(dtbpe)MR_2Li(OR_2)_x$ are significant differences between the hydrocarbon ligands in the anionic and neutral complexes are observed. While the C2 and C3 resonances (see Tables I and V) for both the neutral and anionic phenyl and *p*-tolyl complexes occur at nearly identical δ, the C1 resonances in $(dtbpe)M(C_6H_4R)_2Li(OEt_2)_x$ consistently occur ca. 15–20 ppm downfield of C1 in $(RC_6H_4)M(PMe_3)(dtbpe)$ (comparing the same M and R) while the C4 resonances in the anions occur ca. 2–4 ppm upfield of the value observed for C4 in the neutral complex. The deshielding of C1 in the anionic aryl complexes suggests the ipso carbon bears a substantial negative charge since the chemical shift of C1 in the anion approaches the chemical shift of C1 in the parent aryllithium.[17] Spin–spin coupling between C1 and the phosphorus trans to it, $^2J_{CP}$, is also larger in the anionic complexes than in the neutral complexes. Moreover, the magnitude of this coupling, $^nJ_{CP}$, attenuates more slowly through the intervening aryl carbon–carbon bonds in the anions than it does in the corresponding neutral complexes.[18] This coupling is carbon–phosphorus and not carbon–rhodium since the iridium complexes display it as well.

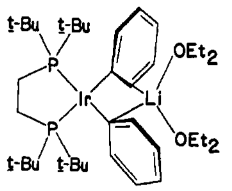


Figure 1. Average solution structure of $(dtbpe)MR_2Li(OR'_2)_x$ shown for the specific case where M = Ir, R = C_6H_5, and R′ = Et. The main structural features are a planar $[(dtbpe)MR_2]^-$ and a tetrahedrally coordinated lithium.

The interaction between the planar $[(dtbpe)MR_2]^-$ and the lithium cation is relatively strong. Attempts to remove the lithium atom from the tight ion-pair $(dtbpe)MR_2Li(OR'_2)_x$, were unsuccessful. When solutions of $(dtbpe)Rh(p\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ are treated with a large excess (10 molar equiv) of bi- or tridentate amines (tmeda, pmdta), amine derivatives such as $(dtbpe)Rh(p\text{-}MeC_6H_4)_2Li(tmeda)$ are isolated. This result also suggests there is substantial negative charge associated with the carbon atoms bound to the transition metal.[19] Since the $(dtbpe)MR_2Li(OR'_2)_x$ complexes are freely soluble in noncoordinating low-dielectric media and since the number of ether or amine ligands coordinated to lithium in these complexes never exceeds two,[20] they cannot be solvent-separated ion pairs. It is reasonable then to assume that the lithium atom in $(dtbpe)MR_2Li(OR'_2)_x$ is not merely a counterion but is intrinsically involved in stabilizing these

---

[10] Anionic hydride and arylhydride complexes of ruthenium(II) have been studied with this concept in mind: (a) Pez, G. P. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1980**, *25*, 399. (b) Grey, R. A.; Pez, G. P. *J. Am. Chem. Soc.* **1980**, *102*, 5948. (c) Grey, R. A.; Pez, G. P.; Wallo, A.; Corsi, J. *J. Chem. Soc., Chem. Commun.* **1980**, *16*, 783. (d) Grey, R. A.; Pez, G. P.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528. (e) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536. (f) Wilczynski, R.; Fordyce, W. A.; Halpern, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 2006. Chan, A. S.; Shieh, H.-S. *J. Chem. Soc., Chem. Commun.* **1985**, 1379.

[11] The reactivity of these anionic ruthenium hydride complexes is significantly higher than the neutral analogue: (a) Grey, R. A.; Pez, G. P. U.S. Patent 4 254 059, 1981. (b) Grey, R. A.; Pez, G. P. U.S. Patent 4 268 454, 1981.

[12] (a) Taube, R.; Honymus, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 261. (b) Rice, G. W.; Tobias, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 2141. (c) Nakazawa, H.; Ozawa, F.; Yamamoto, A. *Organometallics* **1983**, *2*, 241. (d) Sebald, A.; Wrackmeyer, B.; Theocharis, C. R.; Jones, W. *J. Chem. Soc., Dalton Trans.* **1984**, 747.

[13] Del Paggio, A. A.; Muetterties, E. L.; Andersen, R. A., submitted for publication in *Inorg. Chem.*

[14] Several complexes containing the dtbpe ligand have been characterized crystallographically: (a) Del Paggio, A. A.; Andersen, R. A.; Muetterties, E. L., submitted for publication in *Inorg. Chem.* (b) Madigan, M.; Osterberg, C.; Nathan, L.; Ebbinghaus, B., to be submitted for publication in *Acta Crystallogr., Sect C: Cryst. Struct. Commun.* (c) Harada, M.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3472. In all of these structures the cone angle of the phosphine has been determined to be ca. 184 ± 2°.

[15] The halide ligands of $\{(\mu\text{-}Cl)Ir(dtbpe)\}_2$ do not exchange with KI in a variety of polar solvents such as THF or acetone even at reflux, nor are they sufficiently ionic to react with $AgBF_4$ (a bright orange solid which is presumably an Ir–Ag bonded species is formed; it decomposes on standing at room temperature).

[16] Several modifications of the reaction conditions have been employed. These methods included: using solvents of increased polarity (and basicity) such as THF and addition of tmeda to the reaction mixture in order to improve the nucleophilicity of the organolithium reagent. We were unable to cleave the halide bridges of **2** with bases such as pyridine.

[17] By way of comparison, the carbon NMR data for the related complexes *cis*-$(C_6H_5)_2Pt(PEt_3)_2$ (A), *trans*-$(C_6H_5)_2Pt(PEt_3)_2$ (B), and *cis*-$(C_6H_5)ClPt(PEt_3)_2$ (C) are provided: for (A) δ C1 165.0; C2 136.9; C3 127.1; C4 121.0; for (B) δ C1 164.0; C2 140.7; C3 127.4; C4 121.4; for (C) δ C1 157.9; C2 136.2; C3 127.2; C4 122.4. Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981; pp 110–111.

[18] Alternatively one might postulate that these are frequency differences between "supposedly" chemically equivalent carbon atoms C3/C5 and C2/C6 arising as a consequence of $(dtbpe)MR_2Li(OEt_2)_2$ possessing lower symmetry than anticipated (caused perhaps by dimerization in solution). This is unlikely for several reasons. First, the spectra were recorded in a strong donor solvent, THF. Secondly, should any asymmetry occur in solution, it should also be evidenced by the ^1H and/or $^{13}C\{^1H\}$ NMR resonances of the dtbpe methyls and/or quaternary carbons as well as the ^1H NMR resonances of the aryl ligand. Finally, *all* of the chemically inequivalent aryl carbons in **9** show this coupling.

[19] The interaction between the lithium and two ipso carbon atoms is apparently energetically more favorable than interaction of lithium with two sp^3 nitrogens.

[20] With the possible exception of the dimethyl anions, where there is considerably less steric crowding about the lithium atom relative to the aryl anions.

Table I. Representative Multinuclear NMR Data[a]

	^{1}H NMR			^{31}P{^{1}H} NMR	
4, M = Rh, R = Me ($\mathrm{C_6D_6}$)	3.453 (m, 6.4 H)		$\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$	95.39 (d)	$J_{\mathrm{PRh}} = 142.0$
	1.370 (m, 40 H)	$\lvert {}^3J_{\mathrm{HP}} + {}^6J_{\mathrm{HP}} \rvert = 10.4$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}^b$		
	1.320 (m, 6.6 H)		$\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$		
	0.138 (m, 6 H)		$\mathrm{Rh}\mathit{Me}$		
6, M = Rh, R = $\mathrm{C_6H_5}$ (THF-d_8)	7.953 (m, 4 H)		H(ortho)	89.38 (d)	$J_{\mathrm{PRh}} = 128.0$
	6.610 (m, 4 H)		H(meta)		
	6.397 (t, 2 H)	${}^3J_{\mathrm{HH}} = 7.1$	H(para)		
	3.620 (m, 6.5 H)		$\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$		
	1.781 (m, 6.4 H)		$\mathrm{O(CH_2C}\mathit{H}_3\mathrm{)_2}$		
	1.431 (m, 4 H)		$\mathrm{PC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{P}$		
	1.152 (m, 36 H)	$\lvert {}^3J_{\mathrm{HP}} + {}^6J_{\mathrm{HP}} \rvert = 10.2$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}$		
6, M = Rh, R = $\mathrm{C_6H_5}$ ($\mathrm{C_6D_6}$)	8.255 (m, 4 H)		H(ortho)	91.46 (d)	$J_{\mathrm{PRh}} = 128.1$
	6.867 (m, 4 H)		H(meta)		
	6.611 (t, 2 H)	${}^3J_{\mathrm{HH}} = 7.2$	H(para)		
	3.065 (m, 6.5 H)		$\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$		
	1.451 (m, 4 H)		$\mathrm{PC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{P}$		
	1.321 (m, 36 H)	$\lvert {}^3J_{\mathrm{HP}} + {}^6J_{\mathrm{HP}} \rvert = 10.5$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}$		
	1.241 (m, 6.4 H)		$\mathrm{O(CH_2C}\mathit{H}_3\mathrm{)_2}$		
13, M = Ir, R = Me (THF-d_8)	3.519 (m, 8 H)		$\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$	81.90 (s)	
	1.728 (m, 6.6 H)		$\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$		
	1.200 (m, 36 H)	$\lvert {}^3J_{\mathrm{HP}} + {}^6J_{\mathrm{HP}} \rvert = 10.4$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}$		
	1.100 (m, 4 H)		$\mathrm{PC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{P}$		
	0.431 (m, 6 H)		$\mathrm{Ir}\mathit{Me}$		
14, M = Ir, R = $\mathrm{C_6H_5}$ (THF-d_8)	7.699 (m, 4 H)		H(ortho)	81.94 (s)	
	6.852 (m, 4 H)		H(meta)		
	6.462 (t, 2 H)	${}^3J_{\mathrm{HH}} = 7.2$	H(para)		
	3.393 (m, 6.5 H)		$\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$		
	1.272 (m, 4 H)		$\mathrm{PC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{P}$		
	1.169 (m, 36 H)	$\lvert {}^3J_{\mathrm{HP}} + {}^6J_{\mathrm{HP}} \rvert = 10.2$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}$		
	1.122 (m, 6.8 H)		$\mathrm{O(CH_2C}\mathit{H}_3\mathrm{)_2}$		

	^{13}C{^{1}H} NMR		
4, M = Rh, R = Me ($\mathrm{C_6D_6}$)	66.22 (s)		$\mathrm{O(}\mathit{C}\mathrm{H_2CH_2)_2}$
	36.06 (ABX)	$\lvert {}^1J_{\mathrm{CP}} + {}^4J_{\mathrm{CP}} \rvert = 4.0$	$(\mathrm{Me_3}\mathit{C})_2\mathrm{P}^b$
	31.42 (AA′X)	$\lvert {}^2J_{\mathrm{HP}} + {}^5J_{\mathrm{HP}} \rvert = 2.8$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}^b$
	24.97 (s)		$\mathrm{O(CH_2}\mathit{C}\mathrm{H_2)_2}$
	24.95 (ABX)	$\lvert {}^1J_{\mathrm{CP}} + {}^2J_{\mathrm{CP}} \rvert = 33.1$	$\mathrm{P}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2P}$
	−0.85 (ABMX)	${}^2J_{\mathrm{CP}} = 86.9$, ${}^1J_{\mathrm{CRh}} = 24.2$, ${}^2J_{\mathrm{CP}} = 11.5$	RhMe
6, M = Rh, R = $\mathrm{C_6H_6}$ (THF-d_8)	187.57 (ABMX)	${}^2J_{\mathrm{CP}} = 94.0$, ${}^1J_{\mathrm{CRh}} = 37.7$, ${}^2J_{\mathrm{CP}} = 15.7$	C1(ipso)
	142.88 (br d)	${}^3J_{\mathrm{CP}} = 25.0$	C2(ortho)
	125.27 (brd d)	${}^3J_{\mathrm{CP}} = 9.0$	C3(meta)
	119.30 (s)		C4(para)
	66.40 (s)		$\mathrm{O(}\mathit{C}\mathrm{H_2CH_3)_2}$
	36.76 (ABX)	$\lvert {}^1J_{\mathrm{CP}} + {}^4J_{\mathrm{CP}} \rvert = 6.0$	$(\mathrm{Me_3}\mathit{C})_2\mathrm{P}$
	31.94 (AA′X)	$\lvert {}^2J_{\mathrm{CP}} + {}^5J_{\mathrm{CP}} \rvert = 6.0$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}$
	24.88 (ABX)	${}^1J_{\mathrm{CP}} + {}^2J_{\mathrm{CP}} \rvert = 31.3$	$\mathrm{P}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2P}$
	15.82 (s)		$\mathrm{O(CH_2}\mathit{C}\mathrm{H_3)_2}$
13, M = Ir, R = Me (THF-d_8)	68.38 (s)		$\mathrm{O(}\mathit{C}\mathrm{H_2CH_2)_2}$
	35.23 (ABX)	$\lvert {}^1J_{\mathrm{CP}} + {}^4J_{\mathrm{CP}} \rvert = 11.9$	$(\mathrm{Me_3}\mathit{C})_2\mathrm{P}$
	31.43 (AA′X)	$\lvert {}^2J_{\mathrm{CP}} + {}^5J_{\mathrm{CP}} \rvert = 4.5$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}$
	27.10 (ABX)	$\lvert {}^1J_{\mathrm{CP}} + {}^2J_{\mathrm{CP}} \rvert = 35.2$	$\mathrm{P}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2P}$
	26.40 (s)		$\mathrm{O(CH_2}\mathit{C}\mathrm{H_2)_2}$
	1.94 (ABX)	${}^2J_{\mathrm{CP}} = 87.3$, ${}^2J_{\mathrm{CP}} = 6.8$	$\mathrm{Ir}\mathit{Me}$
14, M = Ir, R = $\mathrm{C_6H_6}$ (THF-d_8)	185.90 (ABX)	${}^2J_{\mathrm{CP}} = 94.0$, ${}^2J_{\mathrm{CP}} = 11.3$	C1(ipso)
	142.52 (br d)	${}^3J_{\mathrm{CP}} = 15.1$	C2(ortho)
	124.95 (d)	${}^4J_{\mathrm{CP}} = 13.0$	C3(meta)
	116.91 (d)	${}^5J_{\mathrm{CP}} = 9.1$	C4(para)
	66.40 (s)		$\mathrm{O(}\mathit{C}\mathrm{H_2CH_3)_2}$
	36.08 (ABX)	$\lvert {}^1J_{\mathrm{CP}} + {}^4J_{\mathrm{CP}} \rvert = 13.0$	$(\mathrm{Me_3}\mathit{C})_2\mathrm{P}$
	31.69 (AA′X)	$\lvert {}^2J_{\mathrm{CP}} + {}^5J_{\mathrm{CP}} \rvert = 10.2$	$(\mathit{Me}_3\mathrm{C})_2\mathrm{P}$
	26.84 (ABX)	${}^1J_{\mathrm{CP}}$ v 19.0, ${}^2J_{\mathrm{CP}} = 15.1$	$\mathrm{P}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2P}$
	15.82 (s)		$\mathrm{O(CH_2}\mathit{C}\mathrm{H_3)_2}$

[a] Chemical shifts in ppm; coupling contants in hertz. A complete tabulation of multinuclear NMR data are contained in Tables II–IV in the supplementary material. Spectroscopic comparisons of carbon NMR parameters between the anionic complexes $\mathrm{(dtbpe)MR_2Li(OR'_2)}_x$ and the related neutral species $\mathrm{RM(PMe_3)(dtbpe)}$ (see ref 18) are presented in Table V. [b] Values of ${}^3J_{\mathrm{PP}}$ for the ABX and AA′X systems here ranged between ca. 18 and 22 Hz. The X portions of ABX spectra were obtained for carbon nuclei directly bonded to phosphorus (i.e., isotopically (^{13}C/^{12}C) induced ^{31}P chemical shift differences were significant, converting AA′X spectra into ABX spectra). Likewise, the ipso carbons (those bound directly to the metal center) exhibited ABX spectra.

anionic complexes. On the basis of these considerations, these complexes are assigned the *solution* structure shown in Figure 1 for the specific case of M = Ir, R = $\mathrm{C_6H_5}$, and R′ = Et.

Lithium interactions with anionic late first-row olefin complexes have been studied crystallographically.[4] The coordination environment of lithium in these complexes also involves ancillary ligands (two THF or a single tmeda)

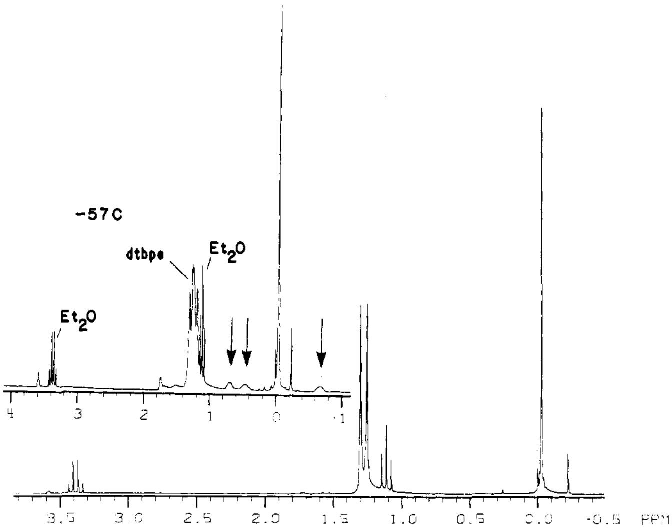


Figure 2. ^{1}H NMR of (dtbpe)Rh(CH_2SiMe_3)$_2$Li(OEt_2)$_{1.5}$ in THF at 22 and −57 °C. The two small resonances at 0 and ca. −0.2 ppm are Me_4Si and an unknown impurity, respectively. Note the dramatic change in the appearance of the dtbpe methyl resonance as well as the appearance of the resonances labeled with an arrow. The initial appearance of the spectrum can be regained by warming the sample back to room temperature.

while the remainder of lithium's coordination sphere is filled by electron-rich carbon atoms. For [(olefin)$_x$M][Li(L)]$_n$ (x = 4, M = Fe,[4i] n = 2, L = tmeda; x = 4, M = Co,[4b] n = 1, L = 2THF; x = 3, M = Ni,[4g] n = 2, L = tmeda; x = 2, M = Ni,[4g] n = 2, L = tmeda) which possesses no *formally* anionic carbon atoms, the lithium atom is within bonding distance of at least one carbon of each of the olefin ligands. When formally anionic carbon atoms *are* present, as in [(η^5-C_5H_5)Fe(olefin)$_2$][Li(tmeda)][4h] or [(olefin)M(C_6H_5)$_2$][Li(L)]$_n$ (M = Ni,[4a] n = 2, L = 2THF; M = Co,[4e] n = 1, L = tmeda), the lithium atom preferentially coordinates to them.[21] In this sense, then, the lithium atom is a convenient solid-state probe for determining sites of high electron density. The existence of direct lithium–transition-metal interactions in these complexes cannot be addressed definitively because coordination of lithium to olefinic and/or *formally* anionic carbon atoms requires it to be within bonding distance of the metal center. The consequences of these interactions are not ordinarily observed by solution NMR spectroscopy at room temperature, although they can frequently be observed in solution at low temperature.[4b] When THF solutions of (dtbpe)Rh(CH_2SiMe_3)$_2$Li(THF)$_{1.5}$ are cooled to −57 °C, the appearance of the dtbpe methyl resonance changes dramatically (see Figure 2). Although the exact reason for this change is unknown, it is possible that the Li(OEt_2)$_x$ unit is interacting at low temperature with the rhodium(I) center, localizing to one side of the rhodium(I) coordination plane. In so doing, the Li(OEt_2)$_x$ unit breaks the C_{2v} symmetry observed at higher temperature, and the dtbpe *tert*-butyl groups become only pairwise (i.e., top is different from bottom) equivalent. With the C_{2v} symmetry removed, the methylene protons of the (trimethylsilyl)methyl ligands become diastereotopic. This would explain the appearance of the resonances highlighted in Figure 2. These resonances are presumably broadened by ^{6}Li, ^{103}Rh, and ^{31}P coupling. The effect of temperature upon the ^{31}P{^{1}H} NMR spectrum is relatively small.

The ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of (dtbpe)RhMe$_2$Li(THF)$_{1.6}$, (dtbpe)Rh(o-MeC_6H_4)$_2$Li(OEt_2)$_{1.6}$, and (dtbpe)Rh(p-MeC_6H_4)$_2$Li(OEt_2)$_{1.6}$ were recorded in solvents of varying basicity and dielectric constant. Comparison of these results shows the general appearance of the spectrum as well as the chemical shifts of the aryl carbon atoms do not change appreciably, giving no evidence to support aggregation of (dtbpe)MR$_2$Li(OR'$_2$)$_x$ in nonpolar solvents. These results also indicate that while the *time-averaged* position of the lithium atom still imparts C_{2v} symmetry to (dtbpe)MR$_2$Li(OEt_2)$_x$, its *instantaneous* disposition remains uncertain. Changes in the coordination environment of Li(OR_2)$_x$ occur either much faster than or much slower than the NMR time scale. In an attempt to address this problem, the ^{1}H and ^{13}C{^{1}H} NMR spectra of (dtbpe)Rh(p-MeC_6H_4)$_2$Li(tmeda)[22] were recorded. In the ^{1}H NMR, the methyl and methylene resonances of the tmeda ligand were broad, indicating exchange between chemically different environments was occurring for the tmeda ligand at a rate comparable to the ^{1}H NMR time scale (see Figure 3). One possible explanation[23] of this phenomenon is the "rocking" motion of the

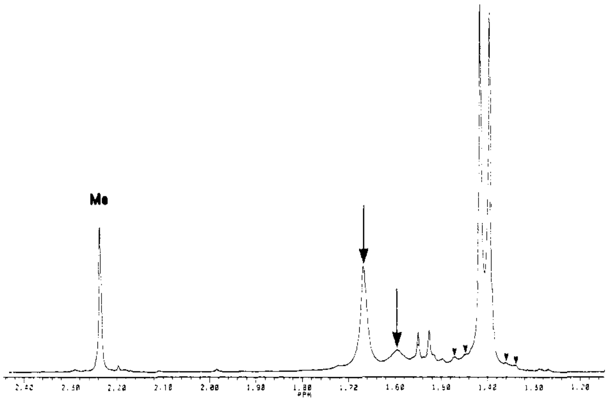


Figure 3. Room-temperature ^{1}H NMR spectrum (C_6D_6) of the complex (dtbpe)Rh(p-MeC_6H_4)$_2$Li(tmeda). The tmeda resonances are marked with the large arrows while the smaller arrows indicate spinning sidebands of the methyl resonance of the dtbpe ligand. The aryl methyl resonance is indicated by "Me".

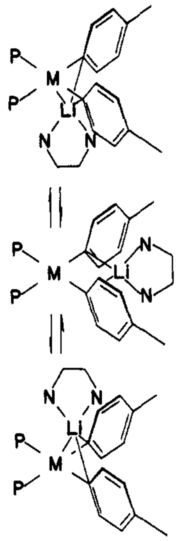


Figure 4. Proposed motion of the Li(tmeda) unit of (dtbpe)Rh(p-MeC_6H_4)$_2$Li(tmeda) in solution. Such a motion occurring at a rate comparable to the NMR time scale would broaden the methyl and methylene resonances of the tmeda ligand. The two aryl protons aresonances are slightly broadened (relative to the diethyl ether solvate) as is the aryl methyl resonance.

---

[21] The lithium coordinates to only one of the cyclopentadienyl ligand in ref 4 h.

[22] Use of tmeda is advantageous since (a) dissociation is unlikely, (b) the ligand is spectroscopically simple, and (c) there are relatively few degrees of freedom associated with the carbon framework of this ligand.

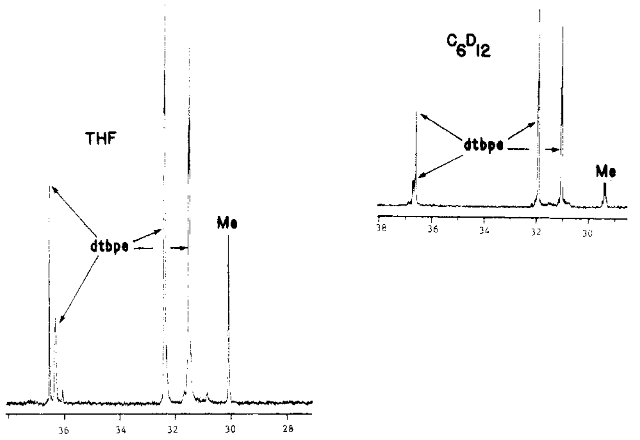


Figure 5. Room-temperature $^{13}C\{^1H\}$ NMR spectrum of (dtbpe)Rh(o-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ in THF-d_8 and cyclohexane-d_{12}. The two dtbpe quaternary resonances occur at ca. 36.5 ppm while the two dtbpe methyl resonances occur at ca. 32.0 ppm; these resonances are labeled "dtbpe". The aryl methyl resonance (Me) displays coupling in cyclohexane whereas in THF this resonance is a sharp singlet.

Li(tmeda) unit along the C1–C1 vector (Figure 4).

Changes occur in the $^{13}C\{^1H\}$ NMR spectra of (dtbpe)Rh(o-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ dissolved in noncoordinating media. As an example, the $^{13}C\{^1H\}$ NMR spectrum of (dtbpe)Rh(o-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ in cyclohexane shows that the aryl methyl resonance displays broad pseudoquartet coupling, perhaps to ^6Li[24] (see Figure 5) although the ^1H resonance of the aryl methyl appears normal. This phenomena is not observed in THF.

Without exception, the complexes (dtbpe)$MR_2Li(OEt_2)_x$ are thermally stable both in the solid state and in solution. Benzene solutions of (dtbpe)$RhMe_2Li(THF)_{1.6}$ are stable at 72 °C; no decomposition was observed by ^1H or $^{31}P\{^1H\}$ NMR spectroscopy after 80 min at this temperature. The high thermal stability of these complexes is surprising because the isoelectronic *cis*-dialkylpalladium(II) and -platinum(II) bis(phosphine) complexes decompose at elevated temperatures via reductive elimination.

Several aspects of the solution behavior of (dtbpe)$MR_2Li(OEt_2)_x$ toward organolithium reagents were explored. Exchange between (dtbpe)$RhMe_2Li(THF)_{1.6}$ and CD_3Li in THF is very slow. No detectable changes in either the ^1H or $^{13}C\{^1H\}$ NMR spectra were observed after 24 h. Likewise, no metathetical exchange (i.e. p-MeC_6H_4 for Me) between (dtbpe)$RhMe_2Li(THF)_{1.6}$ and p-MeC_6H_4Li was observed by ^1H, $^{31}P\{^1H\}$, or $^{13}C\{^1H\}$ NMR spectroscopy after 4 days at room temperature. Similarly, solutions containing two different anions (e.g. (dtbpe)$Rh(CCCMe_3)_2Li(THF)_{0.5}$ and (dtbpe)$Rh(C_6H_5)_2Li(OEt_2)_{1.6}$) do not give spectroscopically observable concentrations of crossover products after standing at room temperature for 24 h. The complexes (dtbpe)$MR_2Li(OR'_2)_x$ are unreactive toward olefin (tenfold excess of C_2H_4, C_2F_4, or allene) and phosphine (1 molar equiv of PMe_3) ligands.

Protonation of (dtbpe)$Ir(C_6H_5)_2Li(OR_2)_{0.8}$ with H_2O affords $\{(\mu$-OH)Ir(dtbpe)$\}_2$ while protonation of (dtbpe)Rh(o-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ with i-PrOH affords $\{(\mu$-H)Rh(dtbpe)$\}_2$. The latter reaction apparently proceeds via a series of proton transfer/reductive elimination sequences ultimately followed by a β-hydride abstraction from the coordinated isopropoxide presumably to generate an anionic alkoxy hydride and acetone. Loss of isopropoxide and dimerization of the resultant "HRh(dtbpe)" fragment afford $\{(\mu$-H)Rh(dtbpe)$\}_2$ which crystallizes from solution. It is likely that this reaction is driven by the gross insolubility of this binuclear hydride.[13,14a] The complex $\{(\mu$-H)Rh(dtbpe)$\}_2$ is also produced by hydrogenolysis of (dtbpe)Rh(o-$MeC_6H_4)_2Li(OEt_2)_{1.6}$. Alkylation of (dtbpe)Rh(o-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ by MeI proceeds rapidly in benzene at room temperature to yield a red, highly insoluble solid that has not been definitively characterized.

Because the complexes (dtbpe)$MR_2Li(OEt_2)_x$ are formally analogous to diorganocuprates in many ways, the alkylation chemistry of the diarylrhodates (dtbpe)$Rh(C_6H_5)_2Li(OEt_2)_{1.6}$ and (dtbpe)Rh(o-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ was briefly explored. Two different types of reactions were investigated. Equations 2a and 2b examine the ability of the arylrhodates to donate an aryl ligand; in (2a) the aryl ligand is donated in exchange for a PMe_3 ligand, and in (2b) it is donated outright. The alkylation reactions shown in eq 2 required several days to proceed to completion.

$$\begin{gathered}(\mathrm{dtbpe})\mathrm{Rh}(o\text{-}\mathrm{MeC_6H_4})_2\mathrm{Li}(\mathrm{OEt_2})_{1.6} + \\ [(\mathrm{Me_3P})_4\mathrm{Rh}]^+\mathrm{Cl}^- \xrightarrow[-\mathrm{LiCl}]{25\ ^\circ\mathrm{C,\ THF}} \\ (o\text{-}\mathrm{MeC_6H_4})\mathrm{Rh}(\mathrm{PMe_3})(\mathrm{dtbpe}) + (o\text{-}\mathrm{MeC_6H_4})\mathrm{Rh}(\mathrm{PMe_3})_3\end{gathered} \tag{2a}$$

$$\begin{gathered}(\mathrm{dtbpe})\mathrm{Rh}(\mathrm{C_6H_5})_2\mathrm{Li}(\mathrm{OEt_2})_{1.6} + \\ \mathrm{ClIr}(\mathrm{PMe_3})(\mathrm{dtbpe}) \xrightarrow[-\mathrm{LiCl}]{25\ ^\circ\mathrm{C,\ THF}} \\ \text{unknown products} + (\mathrm{C_6H_5})\mathrm{Ir}(\mathrm{PMe_3})(\mathrm{dtbpe})\end{gathered} \tag{2b}$$

While both (o-MeC_6H_4)$Rh(PMe_3)$(dtbpe)[13] and (o-$MeC_6H_4)Rh(PMe_3)_3$[25] derived from the alkylation of $[(Me_3P)_4Rh]^+Cl^-$ and the $(C_6H_5)Ir(PMe_3)$(dtbpe)[13] produced by alkylation of $ClIr(PMe_3)$(dtbpe) were identified by comparison of their ^1H and $^{31}P\{^1H\}$ NMR spectra to those of authentic samples, the fate of the alkylating agent in eq 2b remains uncertain.

When the size of the bidentate phosphine is reduced (i.e., dippe is used instead of dtbpe), several differences are observed in the properties of (dippe)Rh(p-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ compared to those of its dtbpe analogue. Although (dippe)Rh(p-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ can be isolated at room temperature, the crystals of this complex are thermally sensitive. Decomposition of this material occurs within 30 min at room temperature as evidenced by a change in color from yellow to brown. Secondly, because the dippe complexes are considerably more soluble in saturated hydrocarbons at low temperatures than their dtbpe analogues, the isolated yield of (dippe)Rh(p-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ is significantly lower. Because the smaller phosphine dippe does not retard the rates of associative reactions as effectively as dtbpe, (dippe)Rh(p-$MeC_6H_4)_2Li(OEt_2)_{1.6}$ exchanges with free p-tolyllithium in solution, at rates comparable to the NMR time scale.

Conclusion

A series of anionic dialkyl-, diaryl-, and dialkynylrhodium(I) and dialkyl-, diaryl-, and dialkynyliridium(I) bis(phosphine) complexes containing the bulky chelating phosphines dtbpe and dippe have been prepared and characterized by using multinuclear NMR spectroscopy. The coordination geometry about the transition-metal center is square-planar. Results obtained from NMR spectroscopy support overall C_{2v} symmetry for the bimetallic complexes (dtbpe)$MR_2Li(OR'_2)_x$ and (dippe)Rh-

---

(23) An alternative explanation might involve interconversion of the tmeda ligand between mono- and bidentate coordination. We have no $^{13}C\{^1H\}$ NMR spectroscopic evidence to support this mechanism, however.

(24) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6391.

(25) Price, R. T. Ph.D. Thesis, University of California, Berkeley, 1986.

(p-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ in solution. Examination of the NMR spectra of (dtbpe)RhR$_2$Li(OR$'_2$)$_x$ (R = Me, C$_6$H$_5$, p-MeC$_6$H$_4$, and o-MeC$_6$H$_4$) in noncoordinating low-dielectric solvents suggests these complexes remain monomeric in solution at room temperature. The ^{13}C{^{1}H} NMR spectrum of (dtbpe)Rh(o-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_2$ suggests that the lithium atom may be interacting with the aryl methyl group when this complex is dissolved in cyclohexane. The anions (dtbpe)MR$_2$Li(OR$'_2$)$_x$ do not react with olefins or PMe$_3$ presumably as a consequence of the high steric demand of the phosphine ligand. Protonation of the anions affords either {(μ-OH)Ir(dtbpe)}$_2$ (using H$_2$O) or {(μ-H)Rh(dtbpe)}^{2} (using i-PrOH). The anions appear to be inert toward exchange of their hydrocarbon ligands. Thus, solutions containing (dtbpe)MR$_2$Li(OR$'_2$)$_x$ and free organolithium do not give evidence of exchange at the NMR time scale. Reaction of (dtbpe)RhMe$_2$Li(THF)$_{1.6}$ with CD$_3$Li gave no indication of crossover after 24 h. Similarly, no redistribution reactions are observed between (dtbpe)MR$_2$Li(OEt$_2$)$_x$ and (dtbpe)MR$'_2$Li(OEt$_2$)$_x$ dissolved in THF, nor are any metathetical reactions observed between (dtbpe)RhMe$_2$Li(THF)$_{1.6}$ and C$_6$H$_5$Li. Like organocuprates, (dtbpe)RhR$_2$Li(OEt$_2$)$_{1.6}$ (R = C$_6$H$_5$, p-MeC$_6$H$_4$) are mild alkylating agents toward certain transition-metal complexes. When the size of the bidentate phosphine is reduced (i.e. dippe vs. dtbpe), several changes in the properties of the ensuing aryl anion are noted. First, the crystals of (dippe)Rh(p-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ are thermally sensitive in the solid state. Secondly, because dippe is not as effective as dtbpe at reducing the rates of associative reactions, (dippe)Rh(p-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ undergoes exchange with free aryllithium in solution.

Experimental Section

All manipulations were performed under dry inert atmospheres employing either standard Schlenk technique or use of a Vacuum Atmospheres drybox. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AM-500 spectrometer, and chemical shifts for these spectra are reported relative to external tetramethylsilane. Phosphorus spectra were recorded at 81.76 MHz on a locally constructed instrument comprised of an Oxford superconducting magnet interfaced with a Nicolet 1180 computer. Chemical shifts for ^{31}P{^{1}H} NMR spectra were initially recorded relative to external trimethyl phosphite and then converted to 85% H$_3$PO$_4$. Positive chemical shifts are at higher frequency than the standard in all cases. Multinuclear NMR data for the compounds (dtbpe)MR$_2$Li(OEt$_2$)$_x$ and (dtbpe)MR$_2$Li(tmeda) (M = Rh, Ir) are contained in Tables I–IV. Virtually coupled AA$'$X[26] and ABX[27] ^{13}C resonances were analyzed according to published methods. The nonintegral ether content in crystalline (dtbpe)MR$_2$Li(OR$'_2$)$_x$ was verified by integration of the ^{1}H NMR spectrum. Microanalyses were performed in the microanalytical laboratory at the University of California, Berkeley.

Preparation of (dtbpe)RhMe$_2$Li(THF)$_{1.6}$ or (dtbpe)Rh(CH$_2$SiMe$_3$)$_2$Li(THF)$_{1.5}$. Into a dry 200 mL Schlenk flask was placed {(μ-Cl)Rh(dtbpe)}$_2$[14a] (600 mg, 1.30 mmol) and a magnetic spin bar. Tetrahydrofuran (ca. 50 mL) was vacuum distilled into the flask at −78 °C: then the flask and its contents were warmed to 0 °C and maintained at that temperature. To the stirred suspension was added 4.4 molar equiv of either MeLi (Fluka, 1.7 M in diethyl ether) or Me$_3$SiCH$_2$Li (freshly prepared; ca. 1 M in Et$_2$O). After the mixture was stirred at 0 °C for ca. 1 h, the ice bath was removed and the suspension was allowed to warm to room temperature. Over the course of several hours the orange {(μ-Cl)Rh(dtbpe)}$_2$ gradually dissolved to yield a homogeneous yellow solution and a precipitate of LiCl. The volatile materials were then removed under reduced pressure to afford a crystalline yellow residue which was extracted with pentane (ca. 50 mL). After the LiCl settled, the clear yellow supernate was transferred to a 100-mL Schlenk tube via cannula. The volume of the extract was reduced to ca. 15 mL (just short of saturation at room temperature) after which the solution was cooled gradually to −80 °C affording yellow crystals of either (dtbpe)RhMe$_2$Li(THF)$_{1.6}$ or (dtbpe)Rh(CH$_2$SiMe$_3$)$_2$Li(THF)$_{1.5}$. The complex (dtbpe)RhMe$_2$Li(THF)$_x$ ($1.6 \leq x \leq 4$), initially obtained as a highly crystalline product, softened at ca. 0 °C. After this material was exposed to dynamic vacuum at 0 °C, the soft crystals hardened affording (dtbpe)RhMe$_2$Li(THF)$_{1.6}$ in 55% yield (448 mg). Crystals of this complex were stable at room temperature. The yellow crystals of (dtbpe)Rh(CH$_2$SiMe$_3$)$_2$Li(THF)$_{1.5}$ initially obtained (570 mg, 62%) did not melt. The THF content in these complexes was determined by integration of the ether resonances with respect to the dtbpe methyl resonance in the ^{1}H NMR spectrum. Anal. Calcd for (dtbpe)RhMe$_2$Li(THF)$_{1.6}$ (C$_{26.4}$H$_{58.8}$LiO$_{1.6}$P$_2$Rh): C, 55.3; H, 10.3. Found: C, 55.5; H, 10.7.

Preparation of (dtbpe)Rh(C$_6$H$_5$)$_2$Li(OEt$_2$)$_{1.6}$, (dtbpe)Rh(p-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$, and (dtbpe)Rh(o-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$. A dry 200-mL Schlenk flask was charged with {(μ-Cl)Rh(dtbpe)}$_2$ (600 mg, 1.30 mmol), 4.4 molar equivs of halide-free aryllithium reagent,[28] and a magnetic spinbar. Diethyl ether (ca. 50 mL) was vacuum distilled onto the reactants at −78 °C; then the flask and its contents were warmed to room temperature and stirred for several hours until all of the {(μ-Cl)Rh(dtbpe)}$_2$ had reacted. Because of the lower nucleophilicity of o-tolyllithium its reaction with {(μ-Cl)Rh(dtbpe)}$_2$ was run at 35 °C; this temperature was maintained until all of the {(μ-Cl)Rh(dtbpe)}$_2$ had dissolved. Unlike the THF solvates, the diethyl ether solvates displayed no tendency to melt when initially isolated. Anal. Calcd for (dtbpe)Rh(p-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ (C$_{38.4}$H$_{66.8}$LiO$_{1.6}$P$_2$Rh): C, 63.3; H, 9.17. Found: C, 63.0; H, 9.02.

Preparation of (dtbpe)Rh(p-MeC$_6$H$_4$)$_2$Li(tmeda). To a solution of (dtbpe)Rh(p-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$ (500 mg, 0.686 mmol) in 30 mL of pentane was added 10 molar equivs of N,N,N',N'-tetramethylethylenediamine (tmeda, 790 mg). After the mixture was left standing overnight at room temperature, the volatile materials were removed under reduced pressure to afford a soft lemon-yellow residue. The residue was exposed to dynamic vacuum for several hours to remove excess tmeda. The residue was dissolved in a minimum amount of pentane (ca. 12 mL), and the solution was gradually cooled to −80 °C. The tmeda solvate (dtbpe)Rh(p-C$_6$H$_4$Me)$_2$Li(tmeda) was obtained in 66% yield (330 mg) as opaque lemon-yellow needles. Anal. Calcd for C$_{38}$H$_{70}$LiN$_2$P$_2$Rh: C, 62.9; H, 9.64. Found: C, 62.7; H, 9.61.

Preparation of (dtbpe)Rh(CCCMe$_3$)$_2$Li(THF)$_{0.5}$. To a solution of LiN(SiMe$_3$)$_2$ (340 mg, 2.00 mmol) in 20 mL of diethyl ether was added freshly distilled (4-Å molecular sieves) *tert*-butylacetylene (200 mg, 2.44 mmol). The solution was stirred at room temperature for 20 min. The volatile materials were removed under reduced pressure to afford colorless crystals of Me$_3$CCCLi(OEt$_2$)$_x$ (2.00 mmol). To this flask was added {(μ-Cl)Rh(dtbpe)}$_2$ (330 mg, 0.750 mmol) and a magnetic spinbar. The flask was evacuated; then 30 mL of diethyl ether was vacuum distilled into it. The suspension of {(μ-Cl)Rh(dtbpe)}$_2$ was heated to 35 °C and stirred at that temperature until all of the orange {(μ-Cl)Rh(dtbpe)}$_2$ had dissolved. After several hours at 35 °C, the homogeneous yellow solution was cooled to room temperature. The volatile materials were removed under reduced pressure to afford a crystalline yellow residue. The residue was extracted with pentane, the suspended LiCl was allowed to settle, and then the clear yellow supernate was transferred to a dry Schlenk tube. The volume of the extract was reduced to ca. 7 mL. Yellow crystals of (dtbpe)Rh(CCCMe$_3$)$_2$Li(THF)$_{0.5}$ were isolated in 65% yield (305 mg) by gradual cooling of the pentane extract to −80 °C. Anal. Calcd for C$_{32}$H$_{62}$LiO$_{0.5}$P$_2$Rh: C, 61.4; H, 9.90. Found: C, 61.2; H, 9.81.

Preparation of (dippe)Rh(p-MeC$_6$H$_4$)$_2$Li(OEt$_2$)$_{1.6}$. To a dry 200 mL Schlenk flask was charged {(μ-Cl)Rh(dippe)}$_2$ (800 mg, 2.00 mmol), p-MeC$_6$H$_4$Li·0.8OEt$_2$ (786 mg, 5.00 mmol, 2.5 molar equivs), and a magnetic spinbar. After the flask was evacuated,

---

(26) (a) Schaefer, T. *Can. J. Chem.* **1962**, *40*, 1678. (b) Nelson, J. H.; Redfield, D. A.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

(27) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: New York, 1967; p 357.

(28) Schlosser, M.; Ladenberger, V. J. *J. Organomet. Chem.* **1967**, *8*, 193.

ca. 75 mL of diethyl ether was distilled into it. The flask and its contents were warmed to −78 °C and stirred at that temperature. Over the course of 2 h the suspension of $\{(\mu\text{-Cl})Rh(dippe)\}_2$ gradually dissolved to yield a homogeneous yellow solution and a white precipitate. The flask was warmed to room temperature and stirred for 30 min. The volatile materials were removed, and the residue was extracted with pentane. After the LiCl and unreacted $p\text{-}MeC_6H_4Li\cdot 0.8OEt_2$ had settled, the clear yellow supernate was transferred to a second dry Schlenk tube via cannula and its volume was reduced to ca. 20 mL. Gradual cooling of this solution to −80 °C afforded $(dippe)Rh(p\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ as thermally sensitive yellow crystals (390 mg, 28%). These crystals can be isolated at room temperature, although they decompose within 30 min at room temperature.

Preparation of $(dtbpe)IrMe_2Li(THF)_2$. A dry 200-mL Schlenk flask was charged with $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$ (500 mg, 1 mmol) and a magnetic spinbar. The flask was evacuated, and ca. 50 mL of THF was vacuum-transferred into the flask at −78 °C. The stirred suspension was allowed to warm to 0 °C, and then 4.4 molar equiv of MeLi was added. After the mixture was stirred at 0 °C for ca. 30 min, the ice bath was removed and the suspension was warmed to room temperature and stirred overnight. The volatile materials were removed under reduced pressure, and the soft crystalline residue was exposed to high vacuum for ca. 1 h. Following extraction of the residue with pentane (ca. 40 mL), the suspended LiCl and unreacted MeLi were allowed to settle over the course of several hours. The clear yellow supernate was transferred to a Schlenk tube via cannula. The volume of the pentane solution was reduced to ca. 10 mL whereupon small crystals of product began to form. The solution was gradually cooled to −80 °C, and yellow crystals of $(dtbpe)IrMe_2Li(THF)_2$ were collected in 48% yield (330 mg). Anal. Calcd for $C_{28}H_{62}O_2LiP_2Ir$: C, 48.7; H, 8.97. Found: C, 48.3; H, 8.69.

Preparation of $(dtbpe)Ir(C_6H_5)_2Li(OEt_2)_{0.8}$ and $(dtbpe)Ir(p\text{-}MeC_6H_4)_2Li(OEt_2)_{0.8}$. A dry 200-mL Schlenk flask was charged with $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$ (500 mg, 1.00 mmol), 4.8 molar equiv of halide-free aryllithium reagent, and a magnetic spinbar. After the flask was evacuated, ca. 50 mL of diethyl ether was distilled into it at −78 °C. The stirred suspension was heated at 35 °C overnight. In certain instances reaction of the aryllithium reagent with $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$ was sluggish, the LiCl produced during the alkylation coated the surface of the unreacted $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$, which prevented it from dissolving. In these instances, the reaction vessel was immersed in a sonicator bath to facilitate reaction. A workup analogous to that described for the dimethyl iridate afforded $(dtbpe)Ir(C_6H_5)_2Li(OEt_2)_{0.8}$ in 28% yield (200 mg) and $(dtbpe)Ir(p\text{-}MeC_6H_4)_2Li(OEt_2)_{0.8}$ in 25% yield (205 mg). Anal. Calcd for $(dtbpe)Ir(C_6H_5)_2Li(OEt_2)_{0.8}$ ($C_{33.2}H_{58}LiO_{0.8}P_2Ir$): C, 54.6; H, 7.94. Found: C, 54.5; H, 7.88. Calcd for $(dtbpe)Ir(p\text{-}MeC_6H_4)_2Li(OEt_2)_{0.8}$ ($C_{35.2}H_{62}LiO_{0.8}P_2Ir$): C, 55.7; H, 8.17. Found: C, 55.5; H, 8.11.

Preparation of $(dtbpe)Ir(CCCMe_3)_2Li(THF)_{0.5}$. Crystals of $Me_3CCCLi(OEt_2)_x$ (1.00 mmol) were prepared in a 200-mL Schlenk flask by the procedure previously described. To this flask was added $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$ (273 mg, 0.500 mmol) and a magnetic spinbar. The flask was evacuated, and 30 mL of diethyl ether was vacuum distilled into it. The stirred suspension of $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$ was heated at 35 °C until all of the yellow $\{(\mu\text{-Cl})Ir(dtbpe)\}_2$ had dissolved. After 12 h at 35 °C, the homogenous yellow solution was cooled to room temperature and the volatile materials were removed under reduced pressure to afford a crystalline yellow residue. After the residue was extracted with pentane and the suspended LiCl was allowed to settle, the clear yellow supernate was transferred to a dry Schlenk tube and the volume of the solution reduced to ca. 5 mL. Gradual cooling of the pentane extract to −80 °C produced 88 mg (25%) of $(dtbpe)Ir(CCCMe_3)_2Li(THF)_{0.5}$ as yellow crystals. Anal. Calcd for $C_{34}H_{62}LiO_{0.5}P_2Ir$: C, 57.1; H, 8.67. Found: C, 57.4; H, 8.73.

Thermal Stability of $(dtbpe)RhMe_2Li(THF)_{1.6}$ in C_6D_6. An apparatus consisting of a 90 °C 4-mm Kontes high-vacuum Teflon stopcock blown directly onto a 5-mm NMR tube was charged with $(dtbpe)RhMe_2Li(THF)_{1.6}$ (50 mg, 0.087 mmol). The tube was evacuated; ca. 0.6 mL of C_6D_6 was distilled into it prior to sealing. The tube was placed into the probe of an NMR spectrometer at room temperature. Both ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded at 22, 40, 55, and 72 °C. The 72 °C ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of $(dtbpe)RhMe_2Li(THF)_{1.6}$ were recorded at 20-min intervals for 80 min. The complex $(dtbpe)RhMe_2Li(THF)_{1.6}$ was stable toward reductive elimination and benzene C–H activation under these conditions (for the time specified).

Reaction of $(dtbpe)Rh(o\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ with H_2. The apparatus described above was charged with $(dtbpe)Rh(o\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ (30 mg, 0.041 mmol). The apparatus was evacuated; then ca. 0.6 mL of THF-d_8 was distilled into it. The headspace was filled with 700 torr of H_2, and the tube was flame-sealed. The tube was shaken while being allowed to warm to room temperature. The presence of H_2 in this sample had a peculiar effect on the ^1H and $^{31}P\{^1H\}$ NMR spectra. In the presence of H_2, the aryl ortho proton resonance as well as the $^{31}P\{^1H\}$ NMR resonance were broadened relative to the parent anion in the absence of hydrogen. The ^1H and $^{31}P\{^1H\}$ NMR spectra of this sample were recorded at −60 °C whereupon they were once again sharp without any peculiar features. No resonances attributable to a hydrido aryl or η^2-H_2 complex were observed. After the mixture was left standing at room temperature under H_2 for ca. 72 h, the initial yellow color of the solution had been discharged and green-black crystals of $\{(\mu\text{-H})Rh(dtbpe)\}_2$[13,14a] had formed on the walls of the NMR tube. An analogous reaction involving D_2 indicated that deuteriation of the aryl methyl group occurred at a rate slightly faster than the deuteriolysis of the Rh–aryl bond.

Reaction of $(dtbpe)Rh(o\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ with *i*-PrOD-d_7. An NMR tube was charged with $(dtbpe)Rh(o\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ (40 mg, 0.055 mmol). The tube was evacuated, and ca. 0.5 mL of C_6D_6 was distilled into it along with 5 molar equiv of *i*-PrOD-d_7 (Aldrich; distilled from 4-Å sieves). Inspection of the NMR tube at daily intervals revealed the initially yellow solution had progressively become brown with the formation of green-black crystals of $\{(\mu\text{-D})Rh(dtbpe)\}_2$. The source of the deuteride ligand was presumably coordinated isopropoxide-d_7. Abstraction of the methine deuterium would yield acetone-d_6 and $\{(\mu\text{-D})Rh(dtbpe)\}_2$.

Reaction of $(dtbpe)Ir(C_6H_5)_2Li(OEt_2)_{0.8}$ with H_2O. An NMR tube was charged with $(dtbpe)Ir(C_6H_5)_2Li(OEt_2)_{0.8}$ (50 mg, 0.068 mmol). The tube was evacuated, and ca. 0.5 mL of C_6D_6 was vacuum distilled into it. Degassed water (3.0 μL, 0.17 mmol) was injected through a rubber septum mounted atop the NMR tube apparatus. The tube was flame-sealed and then warmed to room temperature with gentle agitation. Inspection of the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of this sample indicated: (a) quantitative consumption of starting material; (b) quantitative formation of benzene; (c) overall C_{2v} symmetry (or higher) for the reaction product; (d) the absence of any iridium hydride species. Taken cumulatively, the product of the hydrolysis reaction is assigned as $\{(\mu\text{-OH})Ir(dtbpe)\}_2$. ^1H NMR (20 °C, THF-d_8): δ 1.343 (virtual t, 40 H, $|^3J_{HP} + {}^6J_{HP}| = 12.0$ Hz, $(Me_3C)_2P$ overlapping PCH_2CH_2P), 0.103 (s, 1 H, OH). $^{31}P\{^1H\}$ NMR: δ 74.85 (s).

Reaction of $(dtbpe)RhMe_2Li(THF)_{1.6}$ with CD_3Li. To a 5-mm NMR tube was charged $(dtbpe)RhMe_2Li(THF)_{1.6}$ (50 mg, 0.087 mmol) and $CD_3Li\cdot OEt_2$ (10 mg, 0.1 mmol). The tube was evacuated, and ca. 0.5 mL of THF was distilled into it prior to sealing. Examination of the ^1H NMR spectrum revealed no rapid exchange between free CD_3Li and rhodium-bound CH_3. No crossover products were observed after 24 h.

Reaction of $(dtbpe)RhMe_2Li(THF)_{1.6}$ with $p\text{-}MeC_6H_4Li$. To a 5-mm NMR tube was charged $(dtbpe)RhMe_2Li(THF)_{1.6}$ (50 mg, 0.087 mmol) and $p\text{-}MeC_6H_4Li\cdot 0.8OEt_2$ (16 mg, 0.10 mmol). After the tube had been evacuated and ca. 0.5 mL of THF had been distilled into it, the tube was flame-sealed. Periodic examination of the ^1H and $^{31}P\{^1H\}$ NMR spectra revealed alkyl–aryl crossover had not occurred over 4 days at room temperature.

Reaction of $(dtbpe)Ir(p\text{-}MeC_6H_4)_2Li(OEt_2)_{0.8}$ with $p\text{-}MeC_6H_4Li$. Into an NMR tube was placed $(dtbpe)Ir(p\text{-}MeC_6H_4)_2Li(OEt_2)_{0.8}$ (50 mg, 0.061 mmol) and $p\text{-}MeC_6H_4Li\cdot 0.8OEt_2$. The tube was evacuated, ca. 0.5 mL of THF-d_8 was distilled into it, and then the tube was sealed. Examination of the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of this solution showed no rapid exchange between the "free" and iridium-bound aryl groups.

Reaction of $(dtbpe)Rh(o\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ with $[(Me_3P)_4Rh]^+Cl^-$. An NMR tube was charged with $(dtbpe)Rh(o\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ (40 mg, 0.055 mmol) and $[(Me_3P)_4Rh]^+Cl^-$

Organometallics 1987, *6*, 1267–1275 1267

(25 mg, 0.057 mmol).[29] Following evacuation of the apparatus, ca. 0.6 mL of THF-d_8 was vacuum distilled into it and the tube was flame-sealed. The tube was shaken vigorously while being allowed to warm to ambient temperature. The $[(Me_3P)_4Rh]^+Cl^-$, which is normally insoluble in THF at room temperature, quickly dissolved to afford a homogeneous red solution. Examination of the $^{31}P\{^1H\}$ NMR spectra recorded at daily intervals revealed the disappearance of the two reactants with the appearance of signals attributable to $(o\text{-}MeC_6H_4)Rh(PMe_3)_3$[25] and $(o\text{-}MeC_6H_4)Rh(PMe_3)(dtbpe)$.[13]

Reaction of $(dtbpe)Rh(C_6H_5)_2Li(OEt_2)_{1.6}$ with $ClIr(PMe_3)(dtbpe)$. The NMR tube apparatus described above was charged with $(dtbpe)Rh(C_6H_5)_2Li(OEt_2)_{1.6}$ (40 mg, 0.057 mmol) and $ClIr(PMe_3)(dtbpe)$ (35 mg, 0.057 mmol). The apparatus was evacuated, and then ca. 0.6 mL of THF-d_8 was vacuum distilled into the tube. After the NMR tube was flame-sealed, it was shaken vigorously while being allowed to warm to room temperature. The color of the solution gradually changed from yellow to red. Examination of the $^{31}P\{^1H\}$ NMR spectrum revealed that $(C_6H_5)Ir(PMe_3)(dtbpe)$[13] had been formed. Several other unidentified phosphorus-containing products were also present.

Reaction of $(dippe)Rh(p\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ with $p\text{-}MeC_6H_4Li$. An NMR tube was charged with 50 mg (0.074 mmol) of $(dippe)Rh(p\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ and 20 mg (0.127 mmol) of $p\text{-}MeC_6H_4Li\cdot 0.8OEt_2$. After the tube was evacuated and ca. 0.5 mL of THF-d_8 was vacuum distilled into, it was flame sealed. The $^{13}C\{^1H\}$ NMR spectrum of this sample showed distinct environments for "free" and "rhodium-bound" *p*-tolyllithium, although the resonances were broadened. Coupling information was generally erased except for the aryl ipso resonance which, although very broad, still displayed coupling to the phosphorus trans to it.

Acknowledgment. This work was supported by the National Science Foundation in the form of a research grant (CHE 830-7159) as well as a predoctoral fellowship for AADP.

Registry No. **1**, 107820-53-1; **2**, 107820-59-7; **3**, 107820-57-5; $[(dtbpe)Rh(C_6H_5)_2]li$, 107846-40-2; $[(dtbpe)Rh(p\text{-}MeC_6H_4)_2]Li$, 107820-51-9; $[(dtbpe)Rh(o\text{-}MeC_6H_4)_2]Li$, 107820-52-0; $[(dtbpe)Rh(p\text{-}MeC_6H_4)_2]Li(tMeda)$, 107820-56-4; $[(dippe)Rh(p\text{-}MeC_6H_4)_2]Li$, 107820-56-4; $[(dtbpe)IrMe_2]Ki$, 107820-58-6; $[(dtbpe)Ir(C_6H_5)_2]Li$, 107820-60-0; $[(dthpe)Ir(p\text{-}MeC_6H_4)_2Li$, 107820-61-1; $[(dtbpe)Ir(CCCMe_3)_2]Li$, 107820-62-2; $[(\mu\text{-}D)Rh(dtbpe)]_2$, 107820-63-3; $[(\mu\text{-}H)Rh(dtbpe)]_2$, 107820-64-4; $[(\mu\text{-}OH)IR(dtbpe)]_2$, 107820-64-4; $[(\mu OH)Ir(dtbpe)]_2$, 107820-65-5; $[(Me_3P)4Rh]Cl$, 70525-09-6; $(o\text{-}Me(C_6H_4)Rh(PMe_3)_3$, 77682-07-6; $(o\text{-}Me(C_6H_4)Rh(PMe_3)(dtbpe)$, 107820-66-6; $ClIr(PMe_3)(dtbpe)$, 107820-67-7; $(C_6H_5)Ir(PMe_3)(dtbpe)$, 107820-68-8; $(dtbpe)Ph(CCCMe_3(_2$, 107846-41-3; $[(dtbpe)RhMe_2]Li$, 107820-69-9; $[(dtbpe)Rh(CH_2SiMe_3)_2]Li$, 107820-70-2; PhLi, 591-51-5; $p\text{-}CH_3C_6H_4Li$, 2417-95-0; $o\text{-}CH_3C_6H_4Li$, 6699-93-0; Me_3CCCLi, 37892-71-0; Me_3SiCH_2Li, 1822-00-0; *tert*-butylacetylene, 917-92-0.

Supplementary Material Available: Complete tabulations of ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopic data obtained for the complexes $(dtbpe)MR_2Li(OR'_2)_x$ (M = Rh, Ir), $(dtbpe)Rh(p\text{-}MeC_6H_4)_2Li(tmeda)$, and $(dippe)Rh(p\text{-}MeC_6H_4)_2Li(OEt_2)_{1.6}$ as well as comparisons of carbon NMR parameters between $(dtbpe)MR_2Li(OR'_2)_x$ and $RM(PMe_3)(dtbpe)$ (Tables II–V, respectively) (14 pages). Ordering information is available on any current masthead page.

---

[29] Werner, H.; Fesser, R.; Buchner, W. *Chem. Ber.* **1979**, *112*, 834.

Transition-Metal Organometallic Compounds. 8. Arene Exchange Reactions of Bis(naphthalene)chromium

Benjamin F. Bush, Vincent M. Lynch, and J. J. Lagowski*

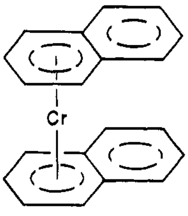
Department of Chemistry, The University of Texas, Austin, Texas 78712

Received October 20, 1986

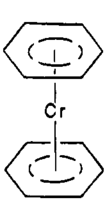
The synthesis and characterization of (η^6-arene)(η^6-naphthalene)chromium and (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium compounds formed in the ligand exchange reaction of bis(η^6-naphthalene)chromium with fluorobenzene, benzene, toluene, mesitylene, and hexamethylbenzene in THF are described. The reaction also produces hydrogenated products, namely, bis(η^6-tetralin)chromium and (η^6-tetralin)(η^6-naphthalene)chromium; these compounds also were independently synthesized and characterized. The ^1H NMR spectra and high-resolution mass spectra used in characterizing the compounds are reported. The X-ray crystal structure of the slipped triple-decker (μ,η^6,η^6-naphthalene)bis(η^6-benzene)dichromium is reported. Although the simple arenes produce only the monoexchange products and the corresponding slipped triple-decker products, dimethyldiphenylsilane yielded the double exchange product bis(η^6-dimethyldiphenylsilane)chromium.

Introduction

Since Timms[1] first reported the direct synthesis of bis(arene)chromium π-complexes from metal atoms and the arene, the process has been used to synthesize a rich profusion of compounds incorporating metal–ligand interactions. We are interested here in the chromium complexes of polycyclic arenes like naphthalene (I) which exhibits distinctly different properties than the conventional arene complexes (II): viz., I undergoes ligand exchange under conditions where II does not.[2] Bis(η^6-naphthalene)chromium can be made through the direct synthetic route either with the conventional co-condensation technique[3,4] or from the evaporation of metal atoms



I



II

---

[1] Timms, P. L. *J. Chem. Soc. D* **1969**, 1033.

[2] Kündig, E. P.; Timms, P. L. J. *Chem. Soc., Dalton Trans.* **1980**, 991.

[3] Elschenbroich, C.; Möckel, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 870.

0276-7333/87/2306-1267$01.50/0 © 1987 American Chemical Society