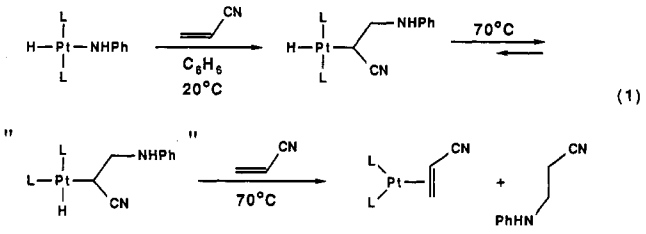
standing for several days or on heating to 150 °C. Insertion products with these unactivated olefins were not detected. Insertion of CO_2, however, proceeds rapidly at room temperature to yield *trans*-PtH(OCONHPh)$(PEt_3)_2$.[19]

Acrylonitrile undergoes a regioselective 1,2-insertion into the Pt–N bond to generate a new hydrido alkyl species, as identified by ^{31}P and ^1H NMR spectroscopies (eq 1).[20]



(1)

The ^{31}P NMR spectrum shows complete conversion of the starting material to the insertion product after 48 h of reaction at room temperature. When the sample is heated to 70 °C for another 48 h, reductive elimination occurs (eq 1) to yield $Pt(PEt_3)_2(\eta^2\text{-}CH_2{=}CHCN)$, as identified by ^{31}P NMR spectroscopy.[21] The organic product 3-anilinopropionitrile was identified by ^1H NMR spectroscopy and by comparison with an authentic sample purchased from Pfaltz and Bauer. The other isomer for the 1,2-addition process could not be detected, so the regioselectivity of addition must be high (>95%). If the reaction between I and acrylonitrile is performed at 70 °C, insertion–reductive elimination is observed with a total reaction time less than 48 h.

Hydrogenolysis of the Pt–N bond of I, eq 2b, also occurs and may proceed by oxidative addition of H_2 to I via an intermediate six-coordinate Pt(IV) species. Consistent

$$PtH_2(PEt_3)_2 \overset{K \approx 1}{\rightleftharpoons} \text{“}Pt(PEt_3)_2\text{”} + H_2 \qquad (2a)$$

$$PtH(NHPh)(PEt_3)_2 + H_2 \overset{K' \gg 1}{\rightleftharpoons} PtH_2(PEt_3)_2 + H_2NPh \qquad (2b)$$

$$PtH(NHPh)(PEt_3)_2 \overset{KK' \gg 1}{\rightleftharpoons} \text{“}Pt(PEt_3)_2\text{”} + H_2NPh \qquad (2c)$$

with this mechanism D_2 adds to I to produce NDHPh, in addition to $PtD_2(PEt_3)_2$ (from ^2H NMR spectral analysis). The equilibrium constant for eq 2b must lie far to the right because addition of a 50-fold excess of aniline to a benzene solution of $PtH_2(PEt_3)_2$[17] led to no detectable reaction. Since reductive elimination of H_2 from $PtH_2(PEt_3)_2$ is favored in the absence of a hydrogen atmosphere (2a),[22] these results require that *trans*-PtH(NHPh)$(PEt_3)_2$ is less thermodynamically stable toward reductive elimination than the dihydride species (eq 2c). Since Pt–N bonds are predicted to be weaker than Pt–H bonds,[9] the kinetic stability of I in solution is unexpected.

Our results show that a hydrido amido complex can be used to model an insertion–reductive elimination sequence, which might be involved in the addition of an N–H bond to an olefin. Unfortunately, as for C–H activation with platinum phosphine complexes[23] oxidative addition of unactivated NH bonds to the intermediate PtL_2 is thermodynamically unfavorable so a catalytic cycle is not completed. The kinetic inertness of the hydrido amido complexes prepared by metathesis may arise from a high barrier to N–H reductive elimination caused by the instability of the cis configuration necessary for reductive elimination. In platinum chemistry, strong trans directors (e.g. H, PR_3, and CH_3) prefer weak trans influence ligands opposite them (e.g. O and N donors).[24] Thus there may be a strong electronic preference for the NHR ligand to be trans to hydride, which shuts down the rate of isomerization, and ultimately leads to a greatly decreased rate of elimination in I. Accelerated reductive elimination on addition of CO or PEt_3 probably occurs by formation of a d^8 trigonal-bipyramidal complex. Molecular orbital theory predicts[25] the strong σ-donor H and PEt_3 ligands should occupy axial sites forcing the axial H and equatorial NHPh ligands into in the required cis geometry for reductive elimination to occur. Alternatively, reductive elimination may proceed by dissociation to free amide and proton transfer.

Acknowledgment. This material is based on work supported by the National Science Foundation (Grant CHE-85-04088). W.C.T. thanks the Alfred P. Sloan Foundation for a research fellowship. We thank Johnson Matthey for a sample of K_2PtCl_4 under their metal loan program.

(18) These products all exhibit ^{31}P NMR (C_6D_6) spectra and Pt–P coupling constants expected[17] for unsaturated molecules symmetrically bound to a zerovalent PtL_2 species: δ 21.0 (s, $^1J_{Pt-P}$ = 3517 Hz, C_2H_4), 12.0 (s, $^1J_{Pt-P}$ = 3301 Hz, C_2Ph_2), 16.5 (s, $^1J_{Pt-P}$ = 3387 Hz, *cis*-HPhC=CPhH). Additional evidence arises from the coupling of ^{195}Pt to the olefinic protons of the ethylene and *cis*-stilbene reaction products. ^1H NMR (C_6D_6): δ 2.1 (s, $^2J_{Pt-H}$ = 57 Hz, C_2H_4), 4.1 (s, $^2J_{Pt-H}$ = 60 Hz, *cis*-HPhC=CPhH).

(19) $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.3 (s, $^1J_{Pt-P}$ = 2854 Hz). ^1H NMR (C_6D_6): δ 9.1 (s, NH), 8.2 (d, ortho), 7.3 (t, meta), 6.9 (t, para), −22.0 (t, Pt–H, $^1J_{Pt-H}$ = 1200 Hz, $^2J_{P-H}$ = 16 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.1 (s, OCONHR). IR (C_6D_6): 1625 cm^{-1} (s, C=O), 2210 cm^{-1} (m, Pt—H). Solutions of this complex are stable only under an atmosphere of CO_2.

(20) $^{31}P\{^1H\}$ NMR (C_6D_6): δ 11.7 (s, $^1J_{Pt-P}$ = 2740 Hz). ^1H NMR (C_6D_6): δ 3.97 (m) and 3.46 (m) (CH_2CN diasteriotopic protons), 4.27 (s, NH), 2.46 (m, $^2J_{Pt-H}$ = 75 Hz, PtCH), −9.54 (t, $^1J_{Pt-H}$ = 785 Hz, $^2J_{P-H}$ = 18 Hz, Pt–H). Anal. Calcd for $C_{21}H_{40}N_2P_2Pt$: C, 43.66; H, 6.99; N, 4.85. Found: C, 44.04; H, 7.30; N, 4.77.

(21) $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.8 ($^1J_{Pt-P}$ = 3299 Hz, $^2J_{P-P}$ = 36 Hz), 18.3 ($^1J_{Pt-P}$ = 3723 Hz, $^2J_{P-P}$ = 36 Hz). For related olefin complexes see ref 17.

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Oxidative Addition/Reductive Elimination of Aldehydes and Ketones at Rhodium. Synthesis and Characterization of Cis Hydrido Acyl Complexes of Rhodium(III)

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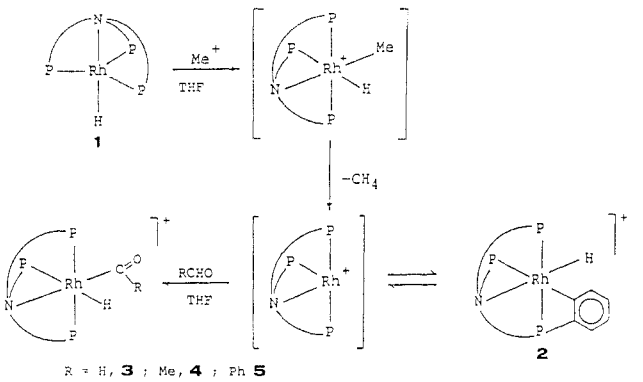
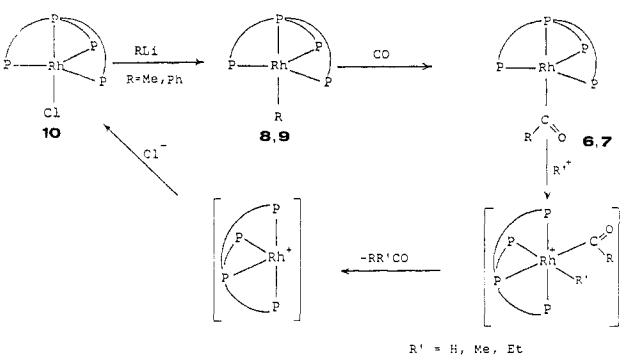
Summary: The Rh(I) complex $(np_3)RhH$ [np_3 = N-$(CH_2CH_2PPh_2)_3$] reacts with Me^+ from $MeOSO_2CF_3$ to give, following the elimination of CH_4, the 16-electron $(np_3)Rh^+$ moiety. The latter reacts with RCHO molecules (R = H, Me, Ph) yielding stable cis hydrido acyl complexes. By contrast, the isoelectronic PP_3Rh^+ system [PP_3 = $P(CH_2CH_2PPh_2)_3$] is unable either to directly activate aldehydes or to keep hydride (or alkyl) and acyl groups in mutually cis positions of the coordination sphere.

0276-7333/87/2306-2453$01.50/0

Scheme I



Scheme II



Several important rhodium-catalyzed processes involve aldehydes either as starting substrates or as intermediates of the catalytic cycles.[1] A key role in many reactions seems to be played by hydrido acyl intermediates produced via metal insertion across sp^2 C–H bonds of RCHO, hence the present, intense interest in the chemistry of the MH(COR) moiety. Unfortunately, very few acyl hydrides have been so far isolated.[2]

The electrophilic attack by Me^+ from $MeOSO_2CF_3$ on the trigonal-bipyramidal monohydride $(np_3)RhH$[3] (**1**) [$np_3 = N(CH_2CH_2PPh_2)_3$] in THF produces a highly unstable cis hydride methyl species which, following the reductive elimination of CH_4, generates the 16-electron $(np_3)Rh^+$ fragment. The latter can be stabilized by appropriate ligands to give trigonal-bipyramidal or octahedral complexes.[4] In the absence of externally added ligands, the ortho-metalated complex $[\{(Ph_2PCH_2CH_2)_2N(CH_2CH_2PPhC_6H_4)\}RhH](SO_3CF_3)$ (**2**) forms through the cleavage of a C–H bond from a phenyl substituent on a phosphine donor.[5] We have now found that the $(np_3)Rh^+$ system, formed in situ as shown in Scheme I, inserts across the C–H bonds from HCHO, MeCHO, or PhCHO to give stable cis hydride acyl derivatives $[(np_3)RhH(COR)]^+$ (R = H, (**3**),[6] Me (**4**),[7] Ph (**5**)[8]). These have been isolated as colorless crystals by addition of $NaBPh_4$ in ethanol to the 1:1:1 mixture of **1**, $MeOSO_2CF_3$, and RCHO in THF. All of the hydrido acyls exhibit octahedral geometries determined by the four donor atoms of np_3 and by two cis H and COR groups. An extremely valid diagnostic tool to determine both the overall geometry of the compounds and the coordination site occupied by the hydride ligands is provided by NMR spectroscopy. In particular, the $^{31}P\{^1H\}$ NMR spectra, invariably exhibiting AM_2X spin systems, are consistent with C_{2v} symmetry of the $(np_3)Rh$ fragment. The hydride ligand lies trans to a phosphorus atom rather than to a nitrogen atom as evidenced by the large value of $J(HP)$ (140–150 Hz).

Interestingly, the isoelectronic $(PP_3)Rh^+$ system that is obtainable in solution by dihydrogen loss from $[(PP_3)Rh(H_2)]^+$[9] does not insert across C–H bonds from aldehydes even under forcible conditions. In order to gain insight into the reasons for this behavior, we have tried to synthesize cis hydride acyl complexes of PP_3 by protonation with $HOSO_2CF_3$ of the trigonal-bipyramidal σ-acyls $(PP_3)Rh(COR)$ (R = Me, (**6**),[10] Ph (**7**)[11]). These are synthesized through carbonylation in THF at room temperature of the trigonal-bipyramidal σ-organyl complexes $(PP_3)RhR$ (R = Me (**8**),[12] Ph (**9**)[13]) obtained by metathetical reaction of $(PP_3)RhCl$ (**10**)[14] with the appropriate organolithium reagent (Scheme II). Invariably, the electrophilic attack by H^+ is followed by the reductive elimination of the aldehyde and the formation of the d^8

(1) See, for example: Tsuji, J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2. Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 50.3. Sneeden, R. P. A *Ibid.*, Chapter 50.2.

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(5) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Sabat, M.; Zanobini, F. *Organometallics* **1986**, *5*, 2557. The mononuclear nature of **2** has been established by an X-ray analysis of the iodide derivative $[(Ph_2PCH_2CH_2)_2N(CH_2CH_2PPhC_6H_4)]RhI]BPh_4$: Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F., manuscript in preparation.

(6) IR (Nujol mulls): ν(Rh–H) 2020, ν(HCO) 1640 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 294 K): AM_2X pattern, $\delta(P_A)$ 14.16 [$J(P_AP_M)$ = 21.5 Hz, $J(P_ARh)$ = 124.2 Hz], $\delta(P_M)$ 33.19 [$J(P_MRh)$ = 106.8 Hz]. ^1H NMR (CD_3COCD_3, 294 K): δ 13.37 (m, HCO, 1 H), –7.39 [ddt, $J(HP_{trans})$ = 139.3 Hz, $J(HP_{cis})$ = 7.0 Hz, $J(HRh)$ = 17.1 Hz, PRhH, 1 H]. Anal. Calcd for $C_{67}H_{64}BNOP_3Rh$: C, 72.76; H, 5.83; N, 1.26; Rh, 9.30. Found: C, 72.24; H, 5.90; N, 1.30; Rh, 9.05.

(7) IR (Nujol mulls): ν(Rh–H) 1990, $\nu(CH_3CO)$ 1630 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 294 K): AM_2X pattern, $\delta(P_A)$ 5.93 [$J(P_AP_M)$ = 21.6 Hz, $J(P_ARh)$ = 124.1 Hz], $\delta(P_M)$ 35.32 [$J(P_MRh)$ = 102.9 Hz]. ^1H NMR (CD_3COCD_3, 294 K): δ 1.24 (m, CH_3CO, 3 H), –8.20 [ddt, $J(HP_{trans})$ = 142.0 Hz, $J(HP_{cis})$ = 8.0 Hz, $J(HRh)$ = 18.0 Hz, PRhH, 1 H]. Anal. Calcd for $C_{68}H_{66}BNOP_3Rh$: C, 72.92; H, 5.94; N, 1.25; Rh, 9.18. Found: C, 72.44; H, 5.89; N, 1.32; Rh, 9.01.

(8) IR (Nujol mulls): ν(Rh–H) 2050, ν(PhCO) 1610, 1575 cm^{-1} (phenyl reinforced vibration). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 294 K): AM_2X pattern, $\delta(P_A)$ 3.45 [$J(P_AP_M)$ = 21.9 Hz, $J(P_ARh)$ = 120.1 Hz], $\delta(P_M)$ 31.05 [$J(P_MRh)$ = 100.8 Hz]. ^1H NMR (CD_3COCD_3, 294 K): δ –8.12 [ddt, $J(HP_{trans})$ = 154.3 Hz, $J(HP_{cis})$ = 10.4 Hz, $J(HRh)$ = 16.4 Hz, PRhH, 1 H]. Anal. Calcd for $C_{75}H_{68}BNOP_3Rh$: C, 74.17; H, 5.79; N, 1.18; Rh, 8.70. Found: C, 74.04; H, 5.71; N, 1.02; Rh, 8.66.

(9) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.*, in press.

(10) IR (Nujol mulls): ν(MeCO) 1575 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 294 K): AM_3X pattern, $\delta(P_A)$ 136.35 [$J(P_AP_M)$ = 20.7 Hz, $J(P_ARh)$ = 77.4 Hz], $\delta(P_M)$ 44.39 [$J(P_MRh)$ = 170.3 Hz]. ^1H NMR (CD_2Cl_2, 294 K): δ 2.16 [m, MeCO, 3 H]. Anal. Calcd for $C_{44}H_{45}OP_4Rh$: C, 64.71; H, 5.55; Rh, 12.60. Found: C, 64.04; H, 5.61; Rh, 12.43.

(11) IR (Nujol mulls): ν(PhCO) 1540 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 294 K): AM_3X pattern, $\delta(P_A)$ 136.23 [$J(P_AP_M)$ = 21.8 Hz, $J(P_ARh)$ = 77.0 Hz], $\delta(P_M)$ 44.14 [$J(P_MRh)$ = 167.3 Hz]. Anal. Calcd for $C_{49}H_{47}OP_4Rh$: C, 66.97; H, 5.39; Rh, 11.71. Found: C, 66.84; H, 5.31; Rh, 11.53.

(12) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 294 K): AM_3X pattern, $\delta(P_A)$ 153.22 [$J(P_AP_M)$ = 17.9 Hz, $J(P_ARh)$ = 88.7 Hz], $\delta(P_M)$ 46.38 [$J(P_MRh)$ = 161.4 Hz]. ^1H NMR (CD_2Cl_2, 294 K): δ 0.38 [m, Me, 3 H]. Anal. Calcd for $C_{43}H_{45}P_4Rh$: C, 65.48; H, 5.75; Rh, 13.04. Found: C, 65.34; H, 5.71; Rh, 12.93.

(13) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 294 K): AM_3X pattern, $\delta(P_A)$ 145.25 [$J(P_AP_M)$ = 18.2 Hz, $J(P_ARh)$ = 81.1 Hz], $\delta(P_M)$ 46.60 [$J(P_MRh)$ = 160.8 Hz]. Anal. Calcd for $C_{48}H_{47}P_4Rh$: C, 67.77; H, 5.56; Rh, 12.09. Found: C, 67.54; H, 5.53; Rh, 11.83.

(14) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 294 K): AM_3X pattern, $\delta(P_A)$ 146.18 [$J(P_AP_M)$ = 17.1 Hz, $J(P_ARh)$ = 127.5 Hz], $\delta(P_M)$ 39.68 [$J(P_MRh)$ = 147.3 Hz]. Anal. Calcd for $C_{42}H_{42}ClP_4Rh$: C, 62.35; H, 5.23; Rh, 12.71. Found: C, 62.29; H, 5.11; Rh, 12.59

$(PP_3)Rh^+$ fragment. The latter easily re-forms the starting trigonal-bipyramidal chloride **10** by addition of (PPN)Cl. In a similar way, C–C bond frmation at rhodium occurs when the σ-acyl complexes **6** and **7** are reacted in THF with the alkylating agents $MeOSO_2CF_3$ and $EtOSO_2CF_3$. Instead of the expected cis organyl acyl derivatives, CH_3COCH_3 or the asymmetric ketones $C_2H_5COCH_3$, $CH_3COC_6H_5$, and $C_2H_5COC_6H_5$ quantitatively form (detected by GC) together with the promptly reutilizable 16-electron $(PP_3)Rh$ fragment.

Theoretical and structural investigations are in progress to try to rationalize the different chemistry of the closely related $(np_3)Rh^+$ and $(PP_3)Rh^+$ fragments. An important role in determining the behavior of these systems is certainly played by the nature of the central donor atom of the tripodal ligand, i.e. nitrogen or phosphorus. In particular, while the amine donor easily unfastens as a new, appropriate ligand approaches the metal, no evidence for $P_{central}$–M bond cleavage in PP_3 complexes has so far been reported.[15] In addition, PP_3 is more reluctant than np_3 to form octahedral complexes. As an example, the octahedral cis dihydride $[(PP_3)RhH_2]^+$ easily rearranges to the trigonal-bipyramidal η^2-dihydrogen derivative in ambient temperature solutions whereas $[(np_3)RhH_2]^+$ invariably maintains the cis dihydride structure.[9]

(15) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616 and references therein.

Rapid, Reversible Proton Exchange between Ring and Metal Sites in the Aryne Complexes $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}C_6H_4)$ and Related Derivatives

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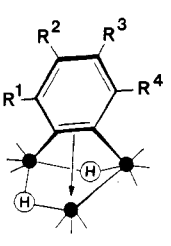
Summary: ^1H NMR spin saturation transfer studies on the complexes $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-aryne})$ (aryne = C_6H_4, C_6H_3Me, and $C_6H_2Me_2$) at ca. 90 °C have established proton transfer between the metal hydride (Os–H–Os) sites and aryne ring (C–H) sites.

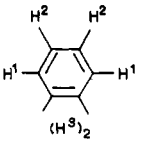
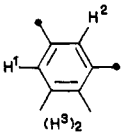
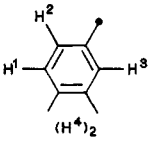
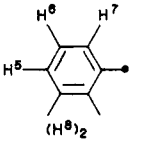
One of the intermolecular C–H bond activation reactions evidenced by the triosmium cluster system is the transformation of simple arenes into the aryne complexes $H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}C_6H_{4-x}R_x)$ (e.g., see **1**–**3**).[1] This reaction



1: $R^1 = R^2 = R^3 = R^4 = H$
2: $R^1 = R^3 = H$, $R^2 = R^4 = Me$
3a: $R^1 = R^2 = R^4 = H$, $R^3 = Me$
3b: $R^1 = R^2 = R^3 = H$, $R^4 = Me$

can be accomplished directly from $Os_3(CO)_{12}$[2] or under milder conditions from $Os_3(CO)_{10}(NCMe)_2$,[3] but intermediates in this obviously multistep process have not been observed. We wish to report the first observation of rapid, reversible exchange between protons bound to the triosmium frame and those on the aryne ring. This observation, conducted by ^1H NMR spin saturation transfer, and the resulting mechanistic interpretation serve to cast light on the pathway of aryne complex formation.

Table I. Spin Saturation Transfer (SST) Experiments[a]

compd[b]	site of irradiation	site of SST effect
 **1**	H^3	H^1
 **2**	H^3	H^1
 **3a**	H^4 H^2	H^1 and H^5 (**3b**) H^3 and H^7 (**3b**)
 **3b**	H^8	H^3 (**3a**)

[a] 500 MHz, CD_3NO_2 solution, +90 °C, PRESAT pulse sequence.[6] [b] Signal assignments based on previous work.[2,3]

The crystal structure of **1** clearly implies that the two hydride ligands occupy inequivalent edges,[3] but in solution separate ^1H NMR signals are observed only at very low temperatures (<–120 °C).[4] The effects of spin saturation transfer become apparent above ca. 80 °C (see Table I).[5] Selective irradiation of the hydride signal in **1** shows a diminution in intensity for just one of the two sets of ring protons. The same result is seen for the dimethyl derivative **2**. The situation is more informative for the monomethyl benzyne complex **3**, which exists as two isomers, a major one, **3a** (ca. 80%), and a minor one, **3b** (ca. 20%). Selective irradiation of the hydride signal in **3a** shows spin transfer not only to one of the adjacent ring protons in **3a** but also to the equivalent site in **3b**. Conversely, irradiating the hydride signal in **3b** reveals spin transfer only to one of the adjacent ring protons in **3a**. These results are uniquely consistent with a process in which the aryne

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(3) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. F. *J. Chem. Soc., Dalton Trans.* **1983**, 2257.

(4) Azam, K. A.; Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1201.

(5) Spin saturation transfer experiments were conducted with the PRESAT pulse sequence[6] on a GE GN-500 FT-NMR spectrometer. The appropriate signal in the ^1H NMR spectrum was irradiated selectively for a period of $>5T_1$, and then the FID was recorded immediately.

(6) Campbell, T. D.; Dobson, C. M.; Ratcliffe, R. G.; Williams, R. F. P. *J. Magn. Reson.* **1978**, *29*, 397.

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