tropic thermal parameters.

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, and additional bond lengths and angles (11 pages); a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

(Benzyne)chromium Tricarbonyl. Preparation and Structure of $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5Cr(CO)_3]\}[\mu_3\text{-}C_6H_4Cr(CO)_3]$ and $Ru_3(CO)_7(\mu_3\text{-}C_6H_4)\{\mu\text{-}PPh[C_6H_5Cr(CO)_3]\}_2$

William R. Cullen,* Steven J. Rettig, and Hongli Zhang

Chemistry Department, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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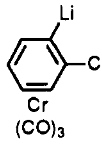
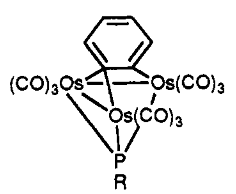
Summary: $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5Cr(CO)_3]\}[\mu_3\text{-}C_6H_4Cr(CO)_3]$ (2) is prepared by reacting $Ru_3(CO)_{12}$ with $PhP[C_6H_5Cr(CO)_3]_2$. The crystal structure shows the aryne moiety, $C_6H_4Cr(CO)_3$, η^2 bound to three Ru atoms that are part of a Ru_3P butterfly arrangement. A Cr→Ru bond is proposed. The P atom is bound to the $C_6H_5Cr(CO)_3$ moiety and three Ru atoms. In contrast, the product of the thermal decomposition of $Ru_3(CO)_{11}PPh_2[C_6H_5Cr(CO)_3]$ is the $\mu_3\text{-}\eta^2$-benzyne complex $Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C_6H_4)\{\mu\text{-}PPh[C_6H_5Cr(CO)_3]\}_2$ (3). Crystals of 2 are monoclinic, with a = 16.918 (2) Å, b = 10.612 (3) Å, c = 19.241 (2) Å, β = 113.64 (2)°, Z = 4, and space group $P2_1/n$, and those of $3\cdot CH_2Cl_2$ are monoclinic, with a = 22.411 (2) Å, b = 17.314 (4) Å, c = 26.191 (4) Å, β = 111.68 (1)°, Z = 8 (two molecules per asymmetric unit), and space group $P2_1/n$. The structures were solved by heavy-atom methods and were refined by full-matrix least-squares procedures to R = 0.043 and 0.037 for 6096 and 10 119 reflections with $I \geq 3\sigma(I)$, respectively.

The possible existence of (benzyne)chromium tricarbonyl has been investigated by Semmelhack and Ullenius,[1] who claimed that the thermal decomposition of the reasonably stable lithio derivative 1 proceeded at 0 °C, with elimination of lithium chloride to provide the novel aryne. However, the evidence is not very convincing. We now report that (benzyne)chromium tricarbonyl can be trapped as part of a ruthenium-carbonyl cluster.



1



4

The complex $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5Cr(CO)_3]\}[\mu_3\text{-}C_6H_4Cr(CO)_3]$ (2; Figure 1) is easily prepared in greater than 50% yield by heating $Ru_3(CO)_{12}$ with the tertiary phosphine $PhP[C_6H_5Cr(CO)_3]_2$ (L) in refluxing heptane for 5 h.[2,3]

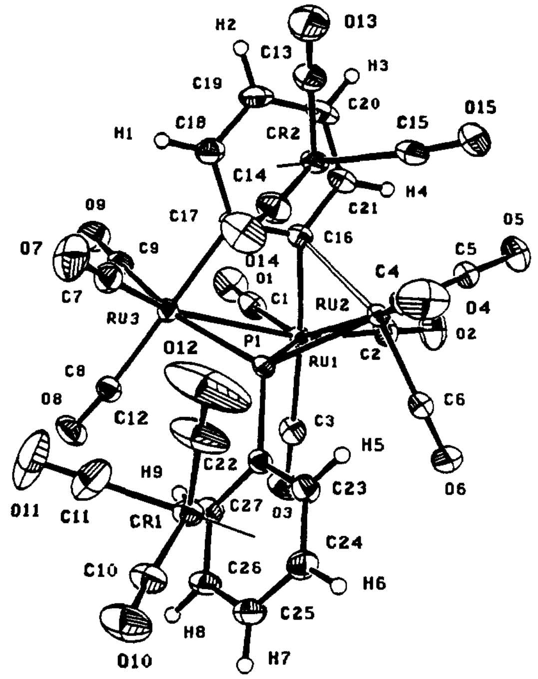


Figure 1. Perspective view of 2 (50% probability thermal ellipsoids are shown for the non-hydrogen atoms).

The other major product is the monosubstituted derivative $Ru_3(CO)_{11}L$. The reaction proceeds slower in refluxing cyclohexane, and TLC monitoring reveals that 2 is formed from $Ru_3(CO)_{11}L$. This thermolysis to produce (benzyne)chromium tricarbonyl is so far unique to ruthenium complexes of $PPh[C_6H_5Cr(CO)_3]_2$.

In contrast, $Ru_3(CO)_{10}\{PPh_2[C_6H_5Cr(CO)_3]\}$ decomposes at 88 °C in heptane to afford $Ru_3(CO)_7(\mu_3\text{-}C_6H_4)\{\mu\text{-}PPh[C_6H_5Cr(CO)_3]\}_2$ (3; Figure 2), a new member of the now well-established class of benzyne derivatives in which the aryne moiety is μ_3,η^2 bound to a M_3 fragment (M = Ru, Os).[3]

The aryne moiety in 2 contains an unsymmetrically bound $Cr(CO)_3$ group; the Cr(2)–C bond lengths range from 2.297 (5) Å for Cr(2)–C(16) to 2.208 (6) Å for Cr-

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[1] Semmelhack, M. F.; Ullenius, C. *J. Organomet. Chem.* **1982**, *235*, C10.

[2] The thermal decomposition of arylphosphine derivatives of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is known to lead to clusters containing aryne fragments;[3] however, attempts to prepare ferrocyne-containing clusters by this method have not been successful to date.[3a,b]

[3] E.g.: (a) Cullen, W. R.; Chacon, S. T.; Bruce, M. I.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1988**, *7*, 2273. (b) Bruce, M. I.; Shawkataly, O. B.; Snow, M. R.; Tiekink, E. R. T.; Cullen, W. R. *Organometallics* **1990**, *9*, 2910. (c) Bruce, M. I.; Guss, J. M.; Mason, R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1983**, *251*, 261. (d) Deeming, A. J.; Kabir, S. E.; Powell, N. I.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 1529.

0276-7333/91/2310-2965$02.50/0

Table I. Crystallographic Data[a]

compd	2	$3 \cdot CH_2Cl_2$
formula	$C_{27}H_9Cr_2O_{15}PRu_3$	$C_{43}H_{24}Cr_2O_{13}P_2Ru_3 \cdot CH_2Cl_2$
fw	1011.53	1319.87
color, habit	red, prism	black, prism
cryst size, mm	0.20 × 0.38 × 0.44	0.15 × 0.46 × 0.48
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	16.918 (2)	22.411 (2)
b, Å	10.612 (3)	17.314 (4)
c, Å	19.241 (2)	26.191 (4)
β, deg	113.64 (1)	111.68 (1)
V, $Å^3$	3164 (1)	9444 (3)
Z	4	8
$\rho calc$, g/cm^3	2.123	1.856
$F(000)$	1944	5240
μ(Mo Kα), cm^{-1}	21.42	15.98
transmission factors	0.69–1.00	0.68–1.00
scan type	$\omega-2\theta$	ω
scan range (in ω), deg	$0.94 + 0.35 \tan\theta$	$0.85 + 0.35 \tan\theta$
scan rate, deg/min	32	32
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
$2\theta_{max}$, deg	65	55
cryst decay, %	2.2	7.5
total no. of rflns	12322	22926
no. of unique rflns	11984	22367
R_{merge}	0.044	0.031
no. of rflns with $I \leq 3\sigma(I)$	6096	10119
no. of variables	434	1189
R	0.043	0.037
R_w	0.048	0.042
GOF	1.57	1.32
max Δ/σ (final cycle)	0.001	0.06
residual density, $e/Å^3$	−2.09 to +1.16 (near Ru)	−0.65 to +0.68

[a] Conditions and additional refinement details: temperature 294 K; Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 0.71069 Å); graphite monochromator; takeoff angle 6.0°; aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal; stationary background counts at each end of the scan (scan:background time ratio 2:1, up to 8 rescans); $\sigma^2(F^2) = [S^2(C + 4B) + (pF^2)^2]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count, p = 0.03 for 2, 0.04 for 3); function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and GOF $= [\sum(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I \geq 3\sigma(I)$.

Table II. Final Atomic Coordinates (Fractional) and B_{eq} Values ($Å^2$)[a] for 2

atom	x	y	z	B_{eq}
Ru(1)	0.39213 (3)	0.11377 (4)	0.58321 (2)	2.43 (1)
Ru(2)	0.22984 (3)	0.11397 (4)	0.59137 (2)	2.64 (2)
Ru(3)	0.31992 (3)	0.22950 (4)	0.43343 (2)	2.40 (1)
Cr(1)	0.11861 (6)	−0.11062 (9)	0.32111 (5)	3.26 (3)
Cr(2)	0.21546 (6)	0.40320 (9)	0.56833 (5)	3.16 (3)
P(1)	0.25258 (8)	0.0831 (1)	0.48066 (7)	2.22 (4)
O(1)	0.5560 (3)	0.2538 (5)	0.5977 (3)	5.5 (2)
O(2)	0.4673 (3)	0.0558 (6)	0.7530 (3)	6.4 (3)
O(3)	0.4357 (3)	−0.1490 (5)	0.5422 (3)	5.6 (2)
O(4)	0.0353 (3)	0.2106 (5)	0.5425 (4)	7.3 (3)
O(5)	0.2829 (4)	0.1513 (5)	0.7636 (3)	6.6 (3)
O(6)	0.2504 (4)	−0.1652 (5)	0.6238 (3)	5.9 (2)
O(7)	0.1712 (3)	0.3545 (6)	0.3051 (3)	6.7 (3)
O(8)	0.3717 (3)	0.0670 (5)	0.3259 (3)	4.8 (2)
O(9)	0.4640 (3)	0.4103 (5)	0.4370 (3)	5.2 (2)
O(10)	−0.0247 (3)	−0.2316 (5)	0.1908 (3)	6.5 (2)
O(11)	0.1682 (5)	0.0444 (8)	0.2153 (4)	10.6 (4)
O(12)	−0.0086 (6)	0.0833 (9)	0.3211 (5)	15.9 (5)
O(13)	0.0889 (4)	0.6130 (5)	0.5417 (4)	6.8 (3)
O(14)	0.0751 (3)	0.3083 (6)	0.4242 (3)	6.0 (2)
O(15)	0.1375 (4)	0.3564 (5)	0.6813 (3)	6.6 (3)
C(1)	0.4945 (4)	0.1992 (6)	0.5879 (3)	3.8 (2)
C(2)	0.4370 (4)	0.0789 (6)	0.6904 (3)	3.8 (2)
C(3)	0.4216 (4)	−0.0522 (6)	0.5600 (3)	3.4 (2)
C(4)	0.1089 (4)	0.1213 (6)	0.5624 (4)	3.9 (2)
C(5)	0.2639 (4)	0.1401 (6)	0.7010 (4)	3.9 (3)
C(6)	0.2415 (4)	−0.0604 (6)	0.6106 (3)	3.9 (3)
C(7)	0.2274 (4)	0.3088 (6)	0.3525 (4)	3.9 (2)
C(8)	0.3494 (3)	0.1201 (5)	0.3659 (3)	3.0 (2)
C(9)	0.4120 (4)	0.3435 (6)	0.4362 (3)	3.2 (2)
C(10)	0.0311 (4)	−0.1834 (6)	0.2393 (4)	4.0 (2)
C(11)	0.1484 (5)	−0.0149 (8)	0.2557 (5)	6.4 (4)
C(12)	0.0416 (6)	0.0112 (9)	0.3217 (5)	8.5 (4)
C(13)	0.1389 (5)	0.5351 (6)	0.5514 (4)	4.4 (3)
C(14)	0.1293 (4)	0.3388 (7)	0.4806 (4)	4.3 (3)
C(15)	0.1690 (5)	0.3674 (6)	0.6382 (4)	4.3 93)
C(16)	0.3405 (3)	0.2944 (5)	0.5895 (3)	2.8 (2)
C(17)	0.3107 (3)	0.3506 (5)	0.5164 (3)	2.9 (2)
C(18)	0.2936 (4)	0.4828 (6)	0.5084 (4)	3.6 (2)
C(19)	0.3050 (4)	0.5570 (6)	0.5721 (4)	4.3 (3)
C(20)	0.3350 (4)	0.5019 (6)	0.6444 (4)	4.3 (3)
C(21)	0.3511 (4)	0.3730 (6)	0.6523 (3)	3.5 (2)
C(22)	0.2180 (3)	−0.0721 (5)	0.4365 (3)	2.5 (2)
C(23)	0.1452 (4)	−0.1316 (6)	0.4406 (3)	3.2 (2)
C(24)	0.1146 (4)	−0.2483 (6)	0.4048 (3)	3.8 (2)
C(25)	0.1539 (4)	−0.3053 (6)	0.3615 (3)	3.8 (2)
C(26)	0.2263 (4)	−0.2490 (5)	0.3567 (3)	3.5 (2)
C(27)	0.2563 (3)	−0.1330 (5)	0.3925 (3)	3.1 (2)

[a] $B_{eq} = {}^8/_3\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i \cdot \mathbf{a}_j)$.

(2)–C(19), and the Cr(2)–ring centroid distance is 1.751 (3) Å. In contrast, the Cr–C distances in the P-bound $C_6H_5Cr(CO)_3$ moiety show much less variation (2.223 (5)–2.191 (5) Å) and the Cr(1)–ring centroid distance is less at 1.694 (2) Å.

The length of C(17)–C(16) in 2 is 1.422 (8) Å, which is similar to that found for the η^2-bound carbon atoms in the benzyne complex 3 (1.420 (8) Å). The C(17)–Ru(3) distance in 2 is 2.103 (5) Å and is similar to the C(16)–Ru(1) distance of 2.131 (5) Å. Again the Ru–C bond lengths in 3 are comparable at 2.132 (6) and 2.117 (6) Å. The C(16)–Ru(2) interaction in 2 is longer (2.688 (6) Å) than any Ru–C bond length in 3, where the longest is 2.327 (6) Å for Ru(1)–C(15).

In 2 the dihedral angle between the planes of the Ru_3P-butterfly is 132.4° and the angle between the plane of the aryne moiety and the plane Ru(3)Ru(1)P(1) is 81.9°. C(4) and C(5) are close to being coplanar with the plane Ru(1)Ru(2)P(1) giving a square-pyramidal geometry about Ru(2) if long interactions with C(16) and/or Cr(2) (Ru(2)–Cr(2) = 3.097 (1) Å) are ignored. However, such interactions must be considered if the 18-electron rule applies. The related molecule $Ru_3(\mu\text{-}H)[\mu_3\text{-}PPh_2(\eta^1,\eta^5\text{-}C_5H_3)Fe(\eta\text{-}C_5H_4PPh_2)](CO)_8$,[3b] which is the closest that we have been able to get to a ferrocyne complex to date, contains a Fe→Ru bond of length 3.098 (3) Å. In view of the geometry and the electron count, a Cr→Ru bond in 2 seems very likely.[4]

A structure somewhat similar to that of 2 has been described for the molecules $Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PR)$ (4; R = Me, Et, Ph), obtained by heating $Os_3(CO)_{11}PPh_2R$ in refluxing nonane[5] or heptane.[6] The solid-state structure of 4 (R = Et) has been determined, and in this case the

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[4] From a steric point of view it is surprising that the $Cr(CO)_3$ moiety is not on the other side of the aromatic ring pointing "outward". This implies that the orientation found serves a bonding function and reinforces the notion that the aryne donates more than two electrons to the cluster. Some further indirect evidence is provided by the opening of the C(14)–Cr(2)–C(15) angle to 100.2 (3)°. The dihedral angles Ru(3)–C(17)–C(16)–C(21) = 169.6 (4)° and Ru(1)–C(16)–C(17)–C(18) = −164.0 (4)° show that the aryne moiety is not a simple *o*-phenylene derivative.

[5] Brown, S. C.; Evans, J.; Smart, L. *J. Chem. Soc., Chem. Commun.* **1980**, 1021.

[6] Deeming, A. J.; Kabir, S. E.; Powell, N. I.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 1529.

Table III. Final Atomic Coordinates (Fractional) and *B*(eq) Values (Å^2) for $3 \bullet CH_2Cl_2$

atom	*x*	*y*	*z*	*B*(eq)
Ru(1)	0.27386 (2)	0.03443 (3)	0.07193 (2)	3.41 (2)
Ru(2)	0.28543 (2)	0.19485 (3)	0.08161 (2)	3.10 (2)
Ru(3)	0.34076 (3)	0.08989 (3)	0.17462 (2)	3.80 (2)
Ru(4)	0.26967 (2)	0.03629 (3)	0.55318 (2)	3.68 (2)
Ru(5)	0.28818 (2)	0.19275 (3)	0.58178 (2)	3.20 (2)
Ru(6)	0.33452 (3)	0.06831 (3)	0.66204 (2)	4.09 (2)
Cr(1)	0.04296 (5)	0.19454 (7)	−0.03354 (4)	4.81 (5)
Cr(2)	0.51057 (6)	0.33937 (7)	0.17809 (5)	5.41 (5)
Cr(3)	0.04275 (5)	0.20725 (7)	0.46343 (4)	4.54 (5)
Cr(4)	0.52025 (5)	0.31110 (7)	0.69319 (4)	4.82 (5)
Cl(1)	0.3819 (1)	0.0583 (2)	−0.1342 (1)	11.1 (2)
Cl(2)	0.3218 (2)	−0.0712 (2)	−0.2027 (1)	12.9 (2)
Cl(3)	0.3961 (2)	0.0847 (2)	0.3672 (1)	11.0 (2)
Cl(4)	0.3242 (2)	−0.0479 (2)	0.3182 (2)	15.7 (2)
P(1)	0.21195 (7)	0.1220 (1)	0.01097 (6)	3.32 (6)
P(2)	0.36714 (8)	0.2196 (1)	0.16487 (6)	3.41 (6)
P(3)	0.21304 (7)	0.1365 (1)	0.50335 (6)	3.42 (6)
P(4)	0.36817 (8)	0.1989 (1)	0.66802 (6)	3.46 (6)
O(1)	0.2977 (3)	−0.0907 (3)	0.0019 (2)	7.1 (3)
O(2)	0.1619 (3)	−0.0487 (3)	0.0833 (2)	7.4 (3)
O(3)	0.1921 (2)	0.2791 (3)	0.1231 (2)	7.3 (3)
O(4)	0.3150 (3)	0.3188 (3)	0.0131 (2)	7.0 (3)
O(5)	0.3094 (4)	−0.0770 (3)	0.1894 (2)	11.9 (4)
O(6)	0.2482 (3)	0.1383 (4)	0.2311 (2)	9.1 (4)
O(7)	0.4664 (3)	0.0722 (4)	0.2713 (2)	9.3 (3)
O(8)	0.0858 (3)	0.3455 (4)	0.0251 (3)	10.5 (4)
O(9)	−0.0892 (3)	0.2573 (4)	−0.0662 (3)	11.3 (4)
O(10)	0.0504 (4)	0.2680 (5)	−0.1336 (3)	12.1 (5)
O(11)	0.4055 (3)	0.4359 (4)	0.1019 (3)	9.4 (4)
O(12)	0.5993 (3)	0.4525 (4)	0.1558 (3)	9.8 (4)
O(13)	0.5114 (4)	0.4359 (4)	0.2732 (3)	12.2 (5)
O(14)	0.2817 (3)	−0.0696 (3)	0.4658 (2)	8.2 (3)
O(15)	0.1545 (3)	−0.0481 (3)	0.5566 (3)	8.2 (3)
O(16)	0.3312 (3)	0.3271 (3)	0.5306 (2)	7.2 (3)
O(17)	0.1955 (3)	0.2718 (4)	0.6265 (2)	8.8 (3)
O(18)	0.2348 (3)	0.1015 (4)	0.7140 (2)	9.7 (4)
O(19)	0.3005 (4)	−0.1024 (4)	0.6542 (3)	12.1 (5)
O(20)	0.4539 (3)	0.0340 (4)	0.7622 (2)	9.9 (4)
O(21)	−0.0865 (3)	0.2702 (5)	0.4459 (3)	11.7 (4)
O(22)	0.0454 (4)	0.3029 (4)	0.3694 (2)	10.4 (4)
O(23)	0.0918 (3)	0.379 (3)	0.5324 (2)	7.8 (3)
O(24)	0.6141 (3)	0.4170 (4)	0.6741 (3)	10.7 (4)
O(25)	0.5293 (4)	0.4027 (4)	0.7924 (2)	11.4 (4)
O(26)	0.4250 (3)	0.4236 (4)	0.6242 (2)	8.5 (3)
C(1)	0.2865 (3)	−0.0444 (4)	0.0278 (3)	4.7 (3)
C(2)	0.2040 (4)	−0.0159 (4)	0.0782 (3)	5.0 (3)
C(3)	0.2247 (3)	0.2495 (4)	0.0156 (3)	4.7 (3)
C(4)	0.3019 (3)	0.2737 (4)	0.0391 (3)	4.6 (3)
C(5)	0.3165 (5)	−0.0158 (5)	0.1767 (3)	7.5 (4)
C(6)	0.2838 (4)	0.1205 (5)	0.2116 (3)	5.4 (4)
C(7)	0.4188 (4)	0.0776 (4)	0.2362 (3)	5.6 (3)
C(8)	0.0714 (4)	0.2865 (5)	0.0030 (3)	7.0 (4)
C(9)	−0.0375 (4)	0.2342 (5)	−0.0529 (3)	7.1 (4)
C(10)	0.0481 (4)	0.2393 (6)	−0.0936 (4)	7.9 (5)
C(11)	0.4451 (4)	0.3985 (5)	0.1311 (4)	6.4 (4)
C(12)	0.5659 (4)	0.4093 (5)	0.1652 (3)	7.0 (4)
C(13)	0.5097 (5)	0.4006 (5)	0.2357 (4)	8.1 (5)
C(14)	0.3527 (3)	0.1184 (3)	0.0682 (2)	3.3 (2)
C(15)	0.3811 (3)	0.0696 (4)	0.1144 (2)	3.8 (3)
C(16)	0.4288 (3)	0.0171 (4)	0.1140 (3)	5.1 (3)
C(17)	0.4488 (3)	0.0143 (5)	0.0704 (3)	6.1 (4)
C(18)	0.4222 (3)	0.0632 (5)	0.0254 (3)	5.3 (4)
C(19)	0.3741 (3)	0.1127 (4)	0.0239 (2)	4.1 (3)
C(20)	0.1263 (3)	0.1138 (3)	−0.0030 (2)	3.8 (3)
C(21)	0.0123 (3)	0.1271 (4)	0.0390 (3)	4.6 (3)
C(22)	0.0374 (4)	0.1148 (5)	0.0313 (3)	5.9 (4)
C(23)	−0.0040 (4)	0.0898 (5)	−0.0203 (4)	7.0 (4)
C(24)	0.0165 (4)	0.0751 (5)	−0.0623 (3)	6.4 (4)
C(25)	0.0815 (3)	0.0884 (4)	−0.0544 (3)	5.3 (3)
C(26)	0.2129 (3)	0.1254 (4)	−0.0588 (2)	4.1 (3)
C(27)	0.2124 (3)	0.1943 (4)	−0.0834 (3)	5.3 (3)
C(28)	0.2120 (4)	0.1989 (6)	−0.1358 (3)	7.3 (5)
C(29)	0.2116 (5)	0.1331 (7)	−0.1642 (3)	8.0 (5)
C(30)	0.2124 (5)	0.0626 (6)	−0.1399 (3)	8.9 (6)
C(31)	0.2125 (4)	0.0581 (4)	0.0869 (3)	6.1 (4)
C(32)	0.4511 (3)	0.2340 (4)	0.1727 (2)	4.1 (3)
C(33)	0.4987 (3)	0.2402 (4)	0.2252 (3)	5.0 (3)
C(34)	0.5639 (4)	0.2460 (5)	0.2332 (3)	6.5 (4)
C(35)	0.5822 (4)	0.2472 (5)	0.1886 (4)	6.8 (4)
C(26)	0.5362 (4)	0.2424 (4)	0.1350 (3)	6.1 (4)
C(37)	0.4706 (3)	0.2372 (4)	0.1272 (2)	4.6 (3)
C(38)	0.3575 (3)	0.2902 (4)	0.2128 (2)	4.0 (3)
C(39)	0.3677 (3)	0.2722 (4)	0.2667 (3)	5.4 (3)
C(40)	0.3616 (4)	0.3279 (6)	0.3023 (3)	7.2 (5)
C(41)	0.3464 (5)	0.4006 (6)	0.2849 (4)	8.1 (5)
C(42)	0.3368 (4)	0.4198 (5)	0.2312 (4)	7.7 (5)
C(43)	0.3413 (4)	0.3644 (5)	0.1959 (3)	5.7 (4)
C(44)	0.2762 (3)	−0.0309 (4)	0.4991 (3)	5.1 (3)
C(45)	0.1974 (4)	−0.0150 (4)	0.5549 (3)	5.3 (3)
C(46)	0.3122 (3)	0.2789 (4)	0.5498 (3)	4.7 (3)
C(47)	0.2289 (3)	0.2434 (4)	0.6086 (3)	5.2 (3)
C(48)	0.2725 (4)	0.0887 (5)	0.6966 (3)	5.8 (4)
C(49)	0.3089 (5)	−0.0374 (5)	0.6511 (3)	7.4 (5)
C(50)	0.4096 (4)	0.0453 (4)	0.7249 (3)	6.0 (4)
C(51)	−0.0359 (4)	0.2460 (5)	0.4534 (3)	7.2 (5)
C(52)	0.0444 (4)	0.2656 (5)	0.4056 (3)	6.4 (4)
C(53)	0.0751 (3)	0.2932 (5)	0.5070 (3)	5.2 (4)
C(54)	0.5796 (4)	0.3759 (5)	0.6836 (4)	7.4 (5)
C(55)	0.5256 (4)	0.3672 (5)	0.7541 (3)	7.3 (5)
C(56)	0.4605 (4)	0.3795 (4)	0.6503 (3)	5.3 (4)
C(57)	0.3537 (3)	0.1192 (3)	0.5623 (2)	3.5 (2)
C(58)	0.3788 (3)	0.0616 (4)	0.6030 (2)	3.7 (3)
C(59)	0.4256 (3)	0.0102 (4)	0.5991 (3)	5.1 (3)
C(60)	0.4484 (4)	0.0176 (5)	0.5572 (3)	6.2 (4)
C(61)	0.4244 (3)	0.0747 (5)	0.5180 (3)	5.4 (4)
C(62)	0.3772 (3)	0.1239 (4)	0.5191 (2)	4.0 (3)
C(63)	0.1268 (3)	0.1278 (4)	0.4860 (2)	3.9 (3)
C(64)	0.0847 (3)	0.1124 (4)	0.4322 (3)	4.5 (3)
C(65)	0.0198 (4)	0.0948 (4)	0.4207 (3)	5.8 (4)
C(66)	−0.0038 (3)	0.0949 (5)	0.4624 (4)	6.5 (4)
C(67)	0.0363 (4)	0.1103 (4)	0.5163 (3)	5.8 (4)
C(68)	0.1009 (3)	0.1278 (4)	0.5278 (3)	4.7 (3)
C(69)	0.2165 (3)	0.1620 (4)	0.4368 (2)	3.6 (3)
C(70)	0.2158 (4)	0.2375 (4)	0.4242 (3)	6.4 (4)
C(71)	0.2290 (5)	0.2617 (5)	0.3753 (3)	8.4 (5)
C(72)	0.2263 (4)	0.2095 (6)	0.3403 (3)	7.3 (5)
C(73)	0.2256 (5)	0.1333 (6)	0.3512 (3)	7.4 (5)
C(74)	0.2221 (4)	0.1093 (4)	0.4001 (3)	6.4 (4)
C(75)	0.4540 (3)	0.2098 (4)	0.6798 (2)	4.0 (3)
C(76)	0.4996 (3)	0.2092 (4)	0.7336 (2)	5.0 (3)
C(77)	0.5659 (3)	0.2102 (5)	0.7441 (3)	6.4 (4)
C(78)	0.5864 (3)	0.2132 (5)	0.7013 (3)	6.4 (4)
C(79)	0.5420 (4)	0.2162 (4)	0.6468 (3)	5.7 (4)
C(80)	0.4765 (3)	0.2152 (4)	0.6360 (2)	4.5 (3)
C(81)	0.3591 (3)	0.2603 (4)	0.7218 (2)	3.8 (3)
C(82)	0.3513 (3)	0.3385 (4)	0.7139 (3)	5.0 (3)
C(83)	0.3464 (4)	0.3858 (5)	0.7540 (4)	7.4 (5)
C(84)	0.3463 (4)	0.3547 (6)	0.8019 (3)	7.6 (5)
C(85)	0.3524 (4)	0.2780 (6)	0.8106 (3)	7.2 (5)
C(86)	0.3591 (3)	0.2299 (4)	0.7703 (3)	5.6 (4)
C(87)	0.3745 (6)	−0.0429 (7)	−0.1428 (5)	14.9 (8)
C(88)	0.3807 (7)	−0.0180 (9)	0.3719 (5)	19 (1)

bond analogous to C(17)–Ru(3) of **2** is described as having some carbenoid character.[7]

Variable-temperature studies of the NMR spectra of **4** reveal a rocking motion of the benzyne moiety. Such a motion apparently occurs in **2** as well because the ^{1}H NMR spectrum at ambient temperature shows an AA′XX′ pattern for the aryne fragment.

The structure of **3** is very similar to that of the other known ruthenium analogues which have as bridging phosphido groups respectively PPh_2 and PPh_2, PPhFc and PPhFc, and PPh_2 and PPhFc.[3a–c] The benzyne moiety in **3** is planar and makes an angle of 61.5 (2)°, which is in the usual range, with the ruthenium triangle.

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(7) A second example of this open cluster benzyne derivative of ruthenium is $Ru_3(CO)_9(\mu_3\text{-}PFc)(\mu_3\text{-}C_6H_4)$, which is the product of the thermolysis of $Ru_3(CO)_{11}(PPh_2Fc)$.[8]

(8) Cullen, W. R.; Rettig, S. J.; Zheng, T.-C. Unpublished results.

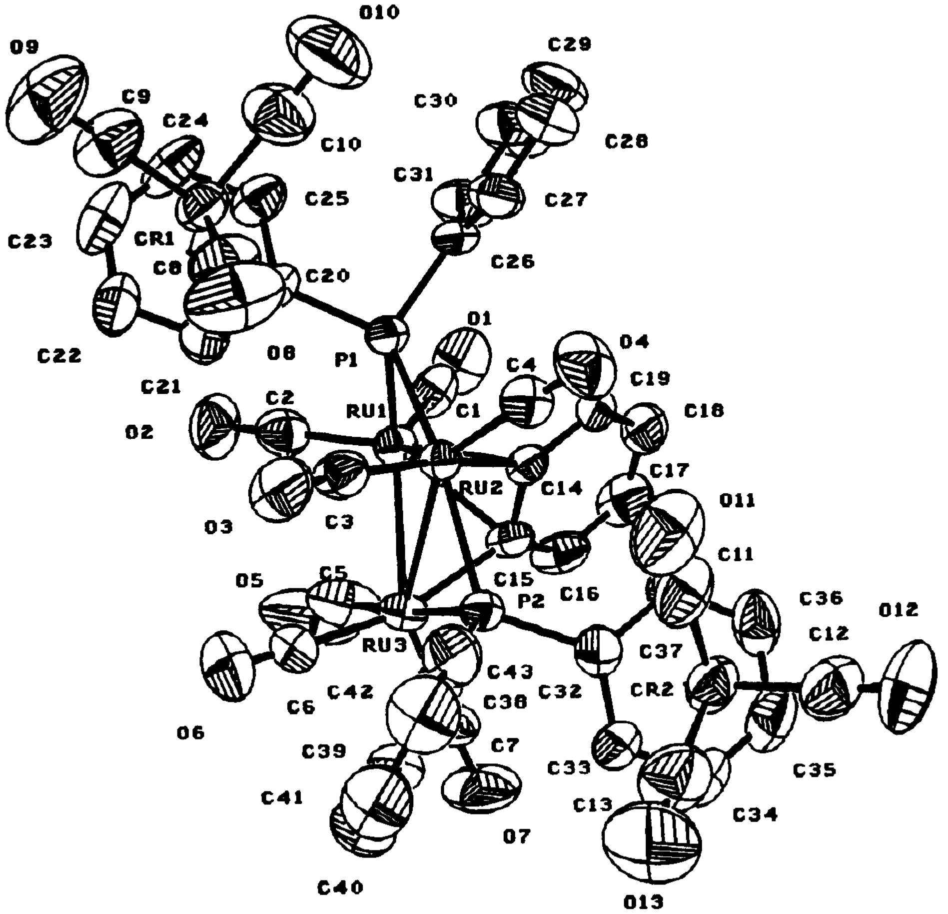

Figure 2. Perspective view of one of the two crystallographically independent molecules of 3 (50% probability thermal ellipsoids are shown for the non-hydrogen atoms).

A sequence of reactions leading to the formation of compounds such as 4 from $Os_3(CO)_{11}PR_2Ar$ has been outlined by Deeming and co-workers.[3d] The first step involves the ortho metalation of the P–Ar ring that ultimately becomes the bound aryne. A similar sequence could account for the production of 2 from $Ru_3(CO)_{11}L$, where there are two incipient (benzyne)chromium tricarbonyl moieties. This scheme has been further elaborated to account for the products of the thermolysis of $Ru_3(CO)_{10}Fe(C_5H_4PPh_2)_2$,[3b] which include a molecule related to 3, and can be invoked to account for the formation of 3 from $Ru_3(CO)_{10}\{PPh_2[C_6H_5Cr(CO)_3]\}_2$ formed by a redistribution reaction of the $Ru_3(CO)_{11}$ derivative.

Experimental Section

Standard Schlenk and vacuum-line techniques were used for the manipulation of air-sensitive substances. Nitrogen was usually used as the inert atmosphere. ^{31}P chemical shifts are reported relative to PPh_3.

Preparation of $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5Cr(CO)_3]\}[\mu_3\text{-}C_6H_4Cr(CO)_3]$ (2). $Ru_3(CO)_{12}$ (180 mg, 0.28 mmol) and $PPh[C_6H_5Cr(CO)_3]_2$ (150 mg, 0.28 mmol) were refluxed in heptane solution (80 mL) for 5 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel (200–400 mesh) with CH_2Cl_2/hexane (1:1.5) as eluent. The product 2 was isolated as a red solid and was recrystallized from CH_2Cl_2/pentane at 4 °C. NMR spectra: $^{31}P\{^1H\}$ (121.4 MHz, $CDCl_3$) δ 406.6; ^1H (300 MHz, $CDCl_3$) δ 4.7 (m, 2 H), 5.2 (m, 3 H), 5.5 (m, 2 H), 5.9 (m, 2 H). Mass spectrum (FAB): m/z 1012 (P^+). Anal. Calcd for $C_{27}H_9Cr_2O_{15}PRu_3$: C, 32.06; H, 0.90. Found: C, 32.02; H, 1.00.

Preparation of $Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C_6H_4)\{\mu\text{-}PPh[C_6H_5Cr(CO)_3]\}_2$ (3). The complex $Ru_3(CO)_{11}PPh_2[C_6H_5Cr(CO)_3]$ (100 mg), prepared from the phosphine and $Ru_3(CO)_{12}$ in a 1:1 molar ratio in THF at room temperature, was refluxed in heptane (30 mL) for 1.5 h. A color change from red to red-brown took place, and TLC monitoring revealed the formation of one principal product. The solvent was removed in vacuo, and the solid residue was chromatographed on alumina (neutral, activity I, 80–200 mesh) with CH_2Cl_2/hexane (1:1.5) as eluent to give a red-purple solid, which was identified as 3, in 40% yield. $Ru_3(CO)_{12}$ of known spectral properties was also isolated in low yield. X-ray-quality crystals of 3 were grown from CH_2Cl_2/hexane at 20 °C. NMR spectra: $^{31}P\{^1H\}$ (121.4 MHz, $CDCl_3$) δ 272.8 (d, J(PP) = 199 Hz), 211.9

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for 2

Bond Distances			
Ru(1)–Ru(2)	2.8123 (7)	Cr(2)–C(18)	2.238 (6)
Ru(1)–Ru(3)	2.9124 (7)	Cr(2)–C(19)	2.208 (6)
Ru(1)–P(1)	2.416 (1)	Cr(2)–C(20)	2.226 (6)
Ru(1)–C(16)	2.131 (5)	Cr(2)–C(21)	2.237 (6)
Ru(2)–P(1)	2.335 (1)	Cr(2)–R(2)[a]	1.751 (3)
Ru(2)–C(16)	2.688 (6)	C(16)–C(17)	1.422 (8)
Ru(2)–Cr(2)	3.097 (1)	C(16)–C(21)	1.419 (7)
Ru(3)–P(1)	2.317 (1)	C(17)–C(18)	1.428 (8)
Ru(3)–C(17)	2.103 (5)	C(18)–C(19)	1.403 (9)
Cr(1)–R(1)[a]	1.694 (2)	C(19)–C(20)	1.40 (1)
Cr(2)–C(16)	2.297 (5)	C(20)–C(21)	1.391 (8)
Cr(2)–C(17)	2.280 (5)		

Bond Angles			
Ru(2)–Ru(1)–Ru(3)	91.34 (2)	Ru(1)–Ru(3)–P(1)	53.57 (3)
Ru(2)–Ru(1)–P(1)	52.38 (3)	Ru(1)–Ru(3)–C(17)	68.7 (2)
Ru(2)–Ru(1)–C(16)	64.2 (1)	P(1)–Ru(3)–C(17)	85.1 (2)
Ru(3)–Ru(1)–P(1)	50.49 (3)	C(13)–Cr(2)–C(14)	83.1 (3)
Ru(3)–Ru(1)–C(16)	70.0 (1)	C(13)–Cr(2)–C(15)	79.1 (3)
P(1)–Ru(1)–C(16)	83.0 (1)	C(14)–Cr(2)–C(15)	100.2 (3)
Ru(1)–Ru(2)–P(1)	55.05 (3)	Ru(1)–P(1)–Ru(2)	72.58 (4)
Ru(1)–Ru(2)–C(16)	45.5 (1)	Ru(1)–C(16)–C(17)	108.1 (4)
P(1)–Ru(2)–C(16)	73.6 (1)	Ru(3)–C(17)–C(16)	113.0 (4)

[a] Here and elsewhere in this report R(1) and R(2) refer to the centroids of the C(22)–C(27) and C(16)–C(21) rings, respectively.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for 3

	Bond Distances		
Ru(1)–Ru(2)	2.793 (1)	Ru(2)–C(14)	2.132 (6)
Ru(1)–Ru(3)	2.7248 (8)	Ru(3)–P(2)	2.360 (2)
Ru(1)–P(1)	2.266 (2)	Ru(3)–C(15)	2.117 (6)
Ru(1)–C(5)	2.696 (8)	C(14)–C(15)	1.420 (8)
Ru(1)–C(14)	2.319 (6)	C(14)–C(19)	1.413 (8)
Ru(1)–C(15)	2.327 (6)	C(15)C(16)	1.405 (8)
Ru(2)–Ru(3)	2.9227 (8)	C(16)–C(17)	1.37 (1)
Ru(2)–P(1)	2.340 (2)	C(17)–C(18)	1.39 (1)
Ru(2)–P(2)	2.311 (2)	C(18)–C(19)	1.366 (9)
	Bond Angles		
Ru(2)–Ru(1)–Ru(3)	63.96 (2)	Ru(1)–Ru(3)–Ru(2)	59.14 (2)
Ru(2)–Ru(1)–C(14)	48.2 (1)	Ru(1)–Ru(3)–C(15)	55.7 (2)
Ru(2)–Ru(1)–C(15)	69.6 (2)	Ru(2)–Ru(3)–C(15)	69.5 (2)
Ru(3)–Ru(1)–C(14)	70.8 (1)	Ru(1)–C(14)–Ru(2)	77.6 (2)
Ru(3)–Ru(1)–C(15)	48.8 (1)	Ru(1)–C(14)–C(15)	72.5 (3)
C(14)–Ru(1)–C(15)	35.6 (2)	Ru(2)–C(14)–C(15)	110.5 (4)
Ru(1)–Ru(2)–Ru(3)	56.89 (2)	Ru(1)–C(15)–Ru(3)	75.5 (2)
Ru(1)–Ru(2)–C(14)	54.2 (2)	Ru(1)–C(15)–C(14)	71.9 (3)
Ru(3)–Ru(2)–C(14)	69.1 (1)		

(d, *J*(PP) = 201 Hz); ^{1}H (300 MHz, CDCl$_3$) δ 4.55 (m, 1), 4.7 (m, 1) 4.8 (m, 1), 5.0 (m, 1), 5.15 (m, 1), 5.25 (m, 1), 5.3–5.4 (m, 2), 5.5 (m, 1), 5.75 (m, 1), 6.4–6.5 (m, 2), 6.5–6.7 (m, 1), 7.08–7.18 (m, 1), 7.42–7.6 (m, 6), 7.6–7.75 (m, 2), 7.88–8.0 (m, 2). IR (FT, CH$_2$Cl$_2$): ν(CO) 2062 (s), 2010 (s), 1975 (s), 1904 (s) cm^{-1}. Mass spectrum (FAB): *m/z* 1216 (P$^+$). Anal. Calcd for Ru$_3$CrP$_2$O$_{13}$C$_{43}$H$_{24}$·CH$_2$Cl$_2$: C, 40.56; H, 2.02. Found: C, 40.52; H, 2.02.

X-ray Crystallographic Analyses. Crystallographic data for $\{\mu_3$-[P(η^6-C$_6$H$_5$)Cr(CO)$_3$]$\}\{\mu_3$-η^3-(η^6-C$_6$H$_4$)Cr(CO)$_3$]$\}$Ru$_3$(CO)$_9$(*2Ru–Ru*) (**2**) and $\{\mu_2$-[PhP(η^6-C$_6$H$_5$)Cr(CO)$_3$]$\}_2$(μ_3-η^2-C$_6$H$_4$)Ru$_3$(CO)$_7$(*3Ru–Ru*)·CH$_2$Cl$_2$ (**3**·CH$_2$Cl$_2$) appear in Table I. The final unit cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 29.8–33.7° for **2** and 27.2–33.4° for **3**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed uniformly by 2.2 and 7.5%, respectively, for **2** and **3**. The data were processed[9] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans for four reflections).

Both structures were solved by heavy-atom methods; the coordinates of the Ru and Cr atoms were determined from subsequent difference Fourier syntheses. All non-hydrogen atoms of both complexes were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). A correction for secondary extinction was applied for **2**, the final value of the extinction coefficient being 1.31×10^{-6}. Neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 10. Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and bond angles appear in Tables II–V.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Stereo ORTEP diagrams and listings of interatomic distances and angles, torsion angles, intermolecular contacts, and least-squares planes for **2** and **3**·CH$_2$Cl$_2$ (65 pages); listings for measured and calculated structure-factor amplitudes (222 pages). Ordering information is given on any current masthead page.

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[9] TEXSAN/TEXRAY structure analysis package, which includes versions of the following: DIRDIF, direct methods for difference structure, by P. T. Beurskens; ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

[10] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Synthesis and Characterization of *trans*-(Me$_3$P)$_2$Pd(C$_6$H$_4$C(H)=NPr^i)(NHPh). X-ray Crystal Structure Analysis of [(Me$_3$P)$_3$Pd(C$_6$H$_4$C(H)=NPr^i)][BF$_4$]

Lawrence A. Villanueva, Khalil Abboud, and James M. Boncella*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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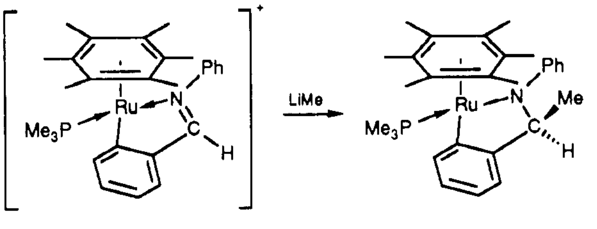
Summary: The reaction of [Pd(C$_6$H$_4$CH=NPr^i)(CH$_3$CN)$_2$][BF$_4$] (**1**) with 3 equiv of PMe$_3$ produces [(Me$_3$P)$_3$Pd(C$_6$H$_4$C(H)=NPr^i)][BF$_4$] (**2**), which was characterized by a single-crystal X-ray diffraction study. Compound **2** was allowed to react with KNHPh in THF at −60 °C to produce *trans*-Pd(C$_6$H$_4$CH=NPr^i)(NHPh)(PMe$_3$)$_2$ (**4**), which was characterized by ^{1}H and ^{31}P NMR spectroscopy.

There has been an increasing interest in the potential use of late-transition-metal (groups 8–10) amide complexes to facilitate the formation of carbon–nitrogen bonds.[1] Consequently, there has been intensified interest in developing new synthetic routes to such compounds. Our attempts to develop new synthetic approaches to late-transition-metal amide complexes have focused on the addition of nucleophiles to cationic, ortho-metalated imine complexes as shown in eq 1.[2]



(1)

Attempts to extend the reaction in eq 1 to ortho-metalated benzaldimine complexes of palladium resulted in displacement of PMe$_3$ from the five-coordinate complex **2**, with preferential attack at the metal center (eq 2). While this unusual displacement of PMe$_3$ by an anionic nucleophile prevents the synthesis of ortho-metalated complexes of palladium analogous to the Ru complexes in

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[1] (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Fryzuk, M. D.; Montgomery, D. C. *Coord. Chem. Rev.* **1989**, *95*, 1–40. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastrava, R. C. *Metal and Metalloid Amides*; Halsted Press: Chatham, Kent, England, 1980; pp 488–533.

[2] Martin, G. C.; Boncella, J. M. *Organometallics* **1989**, *8*, 2968.

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