# Reactivity of the Homoleptic Osmium Aryl $Os(2-MeC_6H_4)_4$: Ligand-Induced Reductive Coupling, $\sigma$- to $\pi$-Rearrangement, and Ortho-Hydrogen Activation

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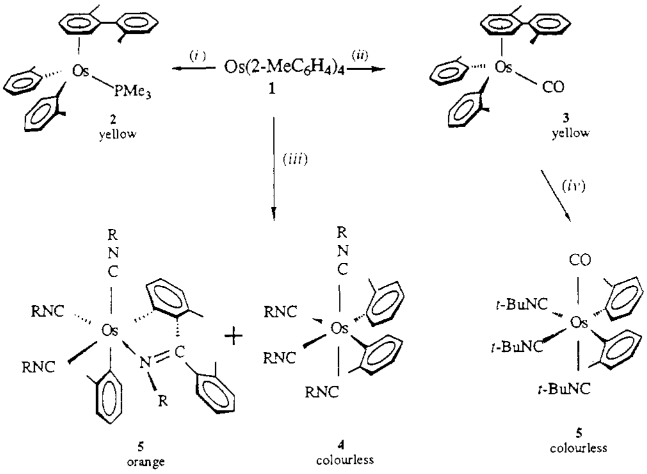
The reactivity of $Os(2-MeC_6H_4)_4$ (**1**) toward Lewis bases has been studied. Reductive coupling in **1** on treatment with $PMe_3$ or CO proceeds with $\sigma$- to $\pi$-rearrangement to the osmium(II) $\eta^6$-biaryl derivatives, $Os[\eta^6\text{-}2\text{-}(2\text{-}MeC_6H_4)MeC_6H_4](2\text{-}MeC_6H_4)_2(L)$ (**2**, L = $PMe_3$; **3**, L = CO). Reaction of **1** with isocyanides yields two osmium(II) species: *cis*-$Os(2-MeC_6H_4)_2(CNR)_4$ (**4a**, R = *t*-Bu; **4b**, R = $2,6-Me_2C_6H_3$) and *fac*-$Os\{C,N\text{-}3\text{-}Me[2\text{-}C(2\text{-}MeC_6H_4)NCMe_3]C_6H_3\}(2\text{-}MeC_6H_4)(CNR)_3$ (**5a**, R = *t*-Bu; **5b** R = $2,6-Me_2C_6H_3$). Treatment of **3** with excess *t*-BuNC gives *cis,fac*-$Os(2-MeC_6H_4)_2(t\text{-}BuNC)_3(CO)$ (**6**). Compounds **2**, **5a**, and **6** have been crystallographically characterized. Crystal data with Mo K$\alpha$ ($\lambda$ = 0.71069 Å) radiation at 291 K are as follows. **2**: monoclinic, space group $P2_1/c$, with *a* = 9.566 (2), *b* = 21.904 (3), *c* = 15.482 (5) Å, $\beta$ = 96.67 (3)°, *Z* = 4, *R* = 0.0327 for 4149 observed data and 327 parameters. **5a**: monoclinic, space group $C2/c$, with *a* = 36.882 (5), *b* = 13.885 (2), *c* = 18.337 (3) Å, $\beta$ = 91.82 (1)°, *Z* = 8, *R* = 0.055 for 2423 observed data and 460 parameters. **6**: monoclinic, space group $P2_1/c$, with *a* = 23.351 (5), *b* = 13.112 (4), *c* = 21.462 (7) Å, $\beta$ = 108.40 (3)°, *Z* = 8 (two independent molecules), *R* = 0.069, for 4609 observed data and 291 parameters.

Recently we described the interaction of tetrakis(2-methylphenyl)rhenium, $Re(2-MeC_6H_4)_4$, with donor ligands,[1] where for phosphines, the aryne derivatives $Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2R)_2$ (R = Me, Ph) are formed evidently by an ortho-hydrogen transfer and elimination of toluene. The molybdenum analogue[2] behaves similarly. We now report reactions of the osmium tetraaryl, $Os(2-MeC_6H_4)_4$ (**1**),[3] with $PMe_3$, CO, and isocyanides.

**Scheme I**[a]



[a] (i) 1 equiv of $PMe_3$, 20 °C. (ii) 1 equiv of CO, 20 °C. (iii) Excess RNC (R = *t*-Bu, $2,6-Me_2C_6H_3$), −80 °C. (iv) Excess *t*-BuNC, 20 °C.

## Results

On addition of 1 equiv of $PMe_3$ (eq i, Scheme I), hexane solutions of $Os(2-MeC_6H_4)_4$ (**1**) slowly (ca. 10 min at 20 °C) turn from maroon to orange-yellow in color. Under similar conditions, but using 10 equiv of $PMe_3$, the reaction is complete within 2 min. Yellow, air-stable crystals of the 18-electron, osmium(II) $\eta^6$-biaryl complex **2** were obtained in 94% yield after recrystallization from diethyl ether.

The molecule is nonrigid in solution at 20 °C as evidenced by the appearance of broad, poorly resolved peaks in the $^1H$ NMR spectrum in toluene-$d_8$ or chloroform-*d*. However, at −60 °C we observe four sharp singlets for the inequivalent methyl groups, together with four distinct multiplets (relative intensity 1:1:1:1) in the region $\delta$ 4–5 ppm for the mono-substituted $\eta^6$-ring of the biaryl. The $PMe_3$ ligand shows a sharp doublet at $\delta$ 0.95 by $^1H$ NMR at −60 °C and a singlet at $\delta$ −47.1 in the $^{31}P\{^1H\}$ NMR spectrum.

The 70-eV mass spectrum of **2** shows peaks due to the biaryl ligand (*m/e* 182) and a peak at *m/e* 167 corresponding to the biaryl–methyl. No osmium-containing peaks were observed. Conclusive evidence for the structure of **2** was obtained by X-ray diffraction (see below).

Arene exchange[4] occurs rapidly when **2** is heated to ca. 100 °C in benzene or toluene (by $^1H$ NMR); the $\eta^6\text{-}C_6H_6$ derivative, isolated from preparative scale reactions, has been fully characterized. In the $^1H$ NMR spectrum, the $\eta^6\text{-}C_6H_6$ ligand shows a sharp doublet (*J* = 0.7 Hz) at $\delta$ 5.24 due to phosphorus coupling. The presence of a molecular plane of symmetry renders the two *o*-tolyls equivalent; these show a singlet at $\delta$ 2.32.

The tetraaryl **1** did not react with $PMe_2Ph$ under conditions similar to eq i (Scheme I); at 60 °C a dark yellow

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(1) (a) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1988**, *704*. (b) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Organometallics* **1989**, *8*, 415.

(2) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.*, in press.

(3) (a) Stavropoulos, P.; Savage, P. D.; Tooze, R. P.; Wilkinson, G.; Hussain, B.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 557. (b) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1988**, 1349.

(4) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 4445 and references therein.

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solution was formed, but attempts to isolate a pure compound failed.

The reaction of 1 in hexane with 1 equiv of carbon monoxide proceeds in an analogous way to that in eq i except that the biaryl complex **3** precipitates as it is formed (eq ii, Scheme I). Although this is stable indefinitely as a solid at 20 °C, it quickly decomposes in benzene or chloroform, even in the presence of excess CO, to unidentified products.

The carbonyl has a strong $\nu_{CO}$ at 1917 cm$^{-1}$ in the IR, while the $^1$H NMR spectrum of a freshly prepared benzene-$d_6$ solution is well-resolved at 20 °C, showing similar features to the spectrum of **2**. Further evidence for the nature of **3** derives from elemental analysis and the X-ray structure of a derivative (see later).

In reactions i and ii of Scheme I above, no evidence was obtained for the formation of isomers of **2** or **3**.

The reaction of **1** with isocyanides is markedly different from reactions with PMe$_3$ and CO. At −80 °C, addition of 4 equiv of RNC (R = *t*-Bu, 2,6-Me$_2$C$_6$H$_3$) to **1** in diethyl ether gave bright yellow-orange solutions, from which two air-stable compounds were separated after several fractional recrystallizations (eq iii, Scheme I). Colorless complexes **4** (**a** and **b**) have been characterized by elemental analysis, MS, and NMR. Both $^1$H and $^{13}$C NMR spectra support a cis structure: the *o*-tolyl ligands are equivalent, but the four isocyanides give rise to two sets of signals of relative intensity 1:1.

The structure of the orange product **5a** from the reaction with *t*-BuNC was determined by X-ray crystallography. Elemental analyses and MS data on both **5a** and **5b** accord with this formulation. However, the 250-MHz $^1$H NMR spectra were exceedingly complex (although temperature invariant from 20–100 °C), and we have not attempted assignments. We suggest that this complexity arises from the presence of various isomers of **5** in solution. Further studies were hampered by the low yields and separation problems encountered.

Repeating reaction iii with <4 equiv of isocyanide led only to the isolation of some unreacted **1** in addition to **4** and **5** in their usual proportions (ca. 2:1). The reaction at higher temperatures (20 or 100 °C) also gave essentially the same ratio of the two products.

In order to test whether an $\eta^6$-arene type intermediate could be involved in the reaction which produces **4**, the CO complex **3** was reacted, as a suspension in hexane, with excess *t*-BuNC (eq iv, Scheme I). High yields of the air-stable, colorless derivative **6** were obtained by crystallization from diethyl ether/hexane.

In addition to the three strong $\nu_{CN}$, there is a strong $\nu_{CO}$ at 1949 cm$^{-1}$. Significantly, both $^1$H and $^{13}$C NMR data show two equivalent *o*-tolyls, but two different types of isocyanide (relative intensity 2:1). These results do not distinguish between the cis,*fac* or trans isomers, but an X-ray diffraction study confirms the cis structure (see below).

Under similar reaction conditions (excess *t*-BuCN in hexane, 20 °C), the PMe$_3$ complex **2** was unreactive.

**Description of the Structures of 2, 5a, and 6.** A diagram of the structure of molecule **2** is shown in Figure 1. The molecule has the well-known $\pi$-arene metal triligand piano-stool structure. The Os–C bond lengths to the two $\sigma$-aryls are equal within experimental error and longer than those in the Os(IV) tetraaryls,[3] as would be expected in view of the different oxidation states. The six atoms of the $\pi$-arene group lie in a plane, the normal of which is tilted by 2° with respect to the metal–centroid vector, largely as a result of steric interactions between substituents on the arene ligand and the legs of the piano stool. The methyl and aryl carbon substituents themselves are only slightly bent out of the arene plane (0.08 and 0.27 Å, respectively).

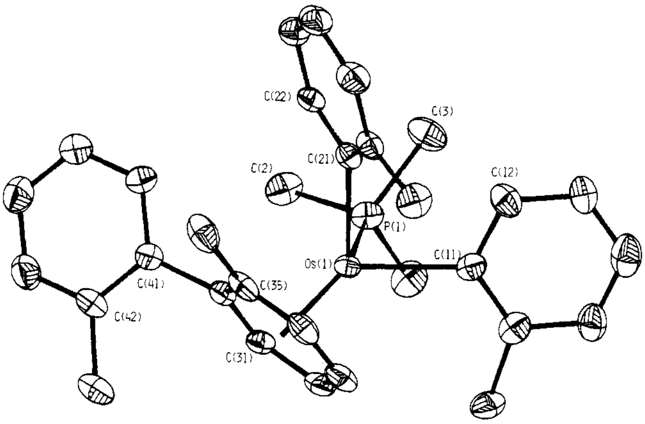

**Figure 1.** The structure of a molecule of **2**.

**Table I. Crystal Data, Details of Intensity Measurements, and Structure Refinement**

| | 2 | 5a | 6 |
|---|---|---|---|
| mol formula | [C$_{31}$H$_{37}$POs] [C$_4$H$_{10}$O]$^a$ | C$_{41}$H$_{56}$N$_4$Os | C$_{37}$H$_{53}$N$_3$Os |
| mol wt | 704.896 | 795.10 | 730.024 |
| cryst system | monoclinic | monoclinic | monoclinic |
| *a*, Å | 9.566 (2) | 36.882 (5) | 23.351 (5) |
| *b*, Å | 21.904 (3) | 13.885 (2) | 13.112 (4) |
| *c*, Å | 15.482 (5) | 18.337 (3) | 21.462 (7) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 96.67 (3) | 91.82 (1) | 108.40 (3) |
| $\gamma$, deg | 90 | 90 | 90 |
| *V*, Å$^3$ | 3221.97 | 9385.76 | 5235.35 |
| space group | $P2_1/c$ | $C2/c$ | $P2_1/c$ |
| *Z* | 4 | 8 | 8 |
| $D_{calcd}$, g cm$^{-3}$ | 1.454 | 1.125 | 1.554 |
| $\mu$, cm$^{-1}$ | 38.92 | 26.18 | 19.68 |
| *F*(000) | 1248 | 3248 | 1367.91 |
| *h,k,l* range | −11→+11, 0→26, −18→+18 | 0→43, 0→16, −21→+21 | −27→+27, 0→15, 0→25 |
| total no. of reflctns | 6059 | 8782 | 11 335 |
| no. of unique reflctns | 5660 | 8258 | 11 009 |
| no. of reflctns used [$F > 3\sigma(F)$] | 4149 | 8090 | 4609 |
| no. of parameters | 327 | 253 | 146 |
| weighting scheme parameter *g* in $w = 1/[\sigma^2(F) + gF_o^2]$ | 0.000 499 | 0.0001 | 0.000 325 |
| final *R* | 0.0327 | 0.0544 | 0.0690 |
| final $R_w$ | 0.0320 | 0.0440 | 0.0665 |

[a] Compound **2** crystallized as a diethyl ether solvate.

These features reflect the steric crowding in the molecule which also correlates with the indications of restricted ligand motions from the NMR studies.

A diagram of a molecule of compound **5a** is shown in Figure 2. The molecule has slightly distorted octahedral geometry with a *fac* arrangement of the three *tert*-butyl isocyanides. The remaining three sites are occupied by one $\sigma$-bonded aryl group and a chelating arylimino ligand. Severe thermal motion and/or disorder in the *tert*-butyl groups complicated the refinement of this structure and the resulting precision is therefore not high. Nevertheless, the geometries within the monodentate *tert*-butyl isocyanide ligands are seen to be normal, with C≡N bond lengths in the range 1.18–1.22 (4) Å. The planarity of C(15) and the C(15)–N(1) distance of 1.30 (2) Å is consistent with the presence of a double bond at this position. The deviations found in Os–C distances to the *tert*-butyl isocyanides are large but suggest that the Os–C bond trans

**Table II. Fractional Atomic Coordinates (×10⁴) for $OsPC_{31}H_{37}$**

| | *x* | *y* | *z* |
|---|---|---|---|
| Os(1) | 566.1 (2) | 1812.1 (1) | 1204.7 (1) |
| P(1) | −684.6 (16) | 1959.6 (9) | 2382.3 (11) |
| C(1) | −2541 (7) | 1755 (4) | 2193 (5) |
| C(2) | −133 (8) | 1505 (4) | 3332 (5) |
| C(3) | −838 (9) | 2713 (4) | 2855 (6) |
| C(11) | −835 (6) | 2526 (3) | 667 (4) |
| C(12) | −497 (7) | 3138 (3) | 864 (5) |
| C(13) | −1312 (8) | 3639 (4) | 580 (5) |
| C(14) | −2580 (8) | 3534 (5) | 67 (6) |
| C(15) | −2970 (7) | 2960 (4) | −138 (5) |
| C(16) | −2154 (6) | 2449 (4) | 146 (4) |
| C(161) | −2815 (7) | 1838 (4) | −142 (5) |
| C(21) | 2108 (6) | 2477 (3) | 1675 (4) |
| C(22) | 2598 (6) | 2496 (3) | 2563 (4) |
| C(23) | 3775 (7) | 2809 (3) | 2925 (5) |
| C(24) | 4562 (7) | 3136 (3) | 2377 (6) |
| C(25) | 4111 (7) | 3142 (3) | 1490 (5) |
| C(26) | 2889 (6) | 2834 (3) | 1134 (4) |
| C(261) | 2493 (8) | 2911 (4) | 168 (5) |
| C(31) | 366 (6) | 808 (3) | 1345 (4) |
| C(32) | −346 (7) | 947 (3) | 524 (4) |
| C(33) | 362 (8) | 1290 (3) | −47 (5) |
| C(34) | 1796 (7) | 1435 (3) | 165 (5) |
| C(35) | 2542 (6) | 1243 (3) | 968 (5) |
| C(36) | 1835 (6) | 913 (3) | 1565 (4) |
| C(351) | 4098 (8) | 1378 (4) | 1139 (6) |
| C(41) | 2575 (6) | 604 (3) | 2360 (4) |
| C(42) | 2584 (7) | −19 (3) | 2417 (5) |
| C(43) | 3228 (8) | −303 (4) | 3166 (5) |
| C(44) | 3897 (10) | 30 (4) | 3844 (6) |
| C(45) | 3921 (10) | 659 (4) | 3781 (6) |
| C(46) | 3260 (7) | 942 (4) | 3042 (5) |
| C(421) | 1893 (11) | −421 (4) | 1685 (6) |
| O(1) | 2010 (12) | 4910 (5) | 2658 (9) |
| C(10) | 1605 (30) | 4587 (11) | 1815 (21) |
| C(20) | 2006 (28) | 4810 (12) | 1166 (17) |
| C(30) | 2850 (27) | 4582 (10) | 3219 (19) |
| C(40) | 3648 (21) | 4804 (10) | 3930 (15) |

to the coordinating imino nitrogen is the shortest. The Os–C distances to the σ-bonded aryls are similar to those in the structure of **2**.

The crystal structure of compound **6** contains two chemically equivalent crystallographically independent molecules which are, however, related by a pseudoglide operation. Figure 3 shows the two molecules and the pseudoglide relationship. As a result of this pseudosymmetry, the refinement was unsatisfactory (see Experimental Section) and the precision of the structure determination low. Nevertheless, the molecular structure is unequivocally defined. It comprises an octahedral metal atom with cis aryls and *fac*-*tert*-butyl isocyanides. The Os–C(aryl) distances lie in the range 2.14–2.16 (3) Å, analogous to the corresponding distances in **2** and **5a**. Unfortunately as with compound **5a**, a large spread in values of Os–C(carbonyl) and Os–C(isocyanide) bond lengths precludes any attempts to identify trans influences.

## Discussion

Reductive coupling and ortho-hydrogen abstraction are the two most common decomposition pathways in metal–aryl chemistry (Scheme II).[5] In reaction of the rhenium[1] and molybdenum[2] tetra-*o*-tolyls with $PMe_3$, mechanism b predominates, and the aryne derivatives $M(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2$ are formed in high yields, with no evidence for reductive coupling. For osmium, however, the reaction follows pathway a, yielding the reductively coupled $\eta^6$-arene complex **2** exclusively.

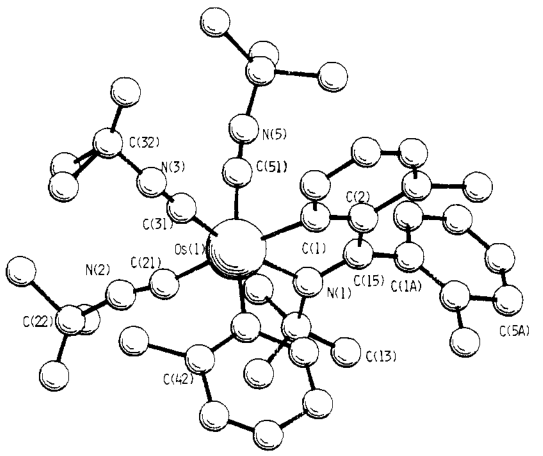

**Figure 2.** The structure of a molecule of **5a**.

**Table III. Fractional Atomic Coordinates (×10⁴) for $C_{41}H_{56}N_4Os$**

| | *x* | *y* | *z* |
|---|---|---|---|
| Os(1) | 1324.5 (2) | 2836.7 (5) | 577.4 (4) |
| N(1) | 1445 (4) | 1791 (9) | −277 (8) |
| C(11) | 1791 (6) | 1186 (12) | −231 (10) |
| C(12) | 1728 (7) | 478 (12) | 403 (11) |
| C(13) | 1892 (7) | 586 (15) | −871 (13) |
| C(14) | 2109 (6) | 1824 (13) | −64 (13) |
| C(15) | 1191 (6) | 1671 (13) | −777 (11) |
| C(1) | 928 (6) | 3105 (14) | −227 (12) |
| C(2) | 897 (6) | 2381 (12) | −789 (10) |
| C(3) | 587 (6) | 2435 (12) | −1292 (11) |
| C(4) | 334 (7) | 3204 (17) | −1214 (15) |
| C(5) | 370 (7) | 3861 (17) | −697 (14) |
| C(6) | 672 (7) | 3855 (15) | −218 (14) |
| C(7) | 528 (6) | 1720 (16) | −1950 (11) |
| C(1A) | 1173 (8) | 930 (14) | −1314 (11) |
| C(2A) | 1026 (7) | 51 (14) | −1094 (16) |
| C(3A) | 1017 (10) | −788 (17) | −1607 (15) |
| C(4A) | 1122 (9) | −565 (22) | −2249 (15) |
| C(5A) | 1283 (9) | 187 (21) | −2534 (17) |
| C(6A) | 1284 (10) | 940 (21) | −1982 (17) |
| C(7A) | 1452 (10) | 1730 (23) | −2330 (18) |
| C(41) | 1671 (7) | 3856 (14) | 61 (12) |
| C(42) | 1917 (7) | 4569 (15) | 403 (15) |
| C(43) | 2140 (9) | 5139 (16) | −34 (19) |
| C(44) | 2119 (9) | 5160 (16) | −731 (18) |
| C(45) | 1889 (9) | 4554 (21) | −1073 (17) |
| C(46) | 1671 (7) | 3925 (14) | −676 (15) |
| C(47) | 1939 (9) | 4710 (17) | 1224 (15) |
| C(21) | 1717 (7) | 2540 (12) | 1309 (12) |
| N(2) | 1906 (6) | 2351 (12) | 1823 (10) |
| C(22) | 2172 (7) | 2059 (20) | 2382 (12) |
| C(23) | 2236 (9) | 959 (20) | 2397 (18) |
| C(24) | 2020 (11) | 2345 (21) | 3093 (13) |
| C(25) | 2453 (8) | 2598 (19) | 2351 (20) |
| C(31) | 1142 (7) | 3684 (14) | 1209 (12) |
| N(3) | 993 (8) | 4233 (18) | 1622 (14) |
| C(32) | 816 (13) | 4488 (26) | 2294 (21) |
| C(33) | 1007 (16) | 4299 (36) | 3035 (16) |
| C(34) | 458 (20) | 5020 (28) | 2321 (45) |
| C(35) | 995 (17) | 5538 (29) | 2577 (28) |
| C(51) | 983 (7) | 1936 (12) | 893 (13) |
| N(5) | 748 (6) | 1394 (15) | 1054 (11) |
| C(52) | 368 (11) | 1073 (24) | 1091 (21) |
| C(53) | 224 (18) | 1606 (31) | 1622 (25) |
| C(54) | 205 (9) | 1157 (21) | 368 (16) |
| C(55) | 385 (12) | 73 (24) | 1223 (23) |

Intramolecular coupling of aryl ligands on transition metals (normally with formation of free biaryl) is well documented.[5-7] Well-defined examples of ligand-induced biaryl eleminations are scarce,[5b,6c] although loss of aryl–R

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(5) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed., Wiley: New York, 1988; p 1131. (b) Collman, J. P.; Hegedus, L.; Norton, J. R.; Finke, R. J. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; p 322. (c) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243.

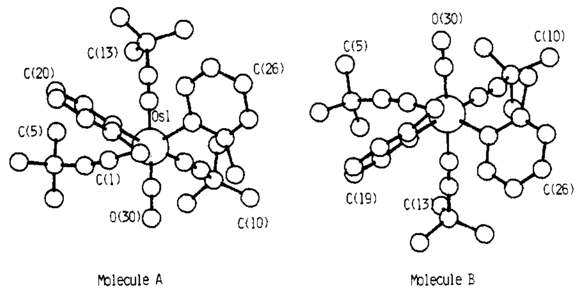
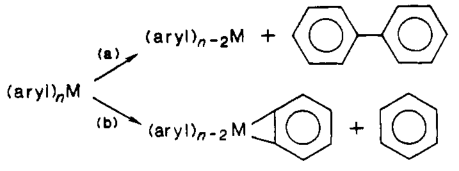


**Figure 3.** The two independent molecules in the structure of **6**; the pseudo *a*-glide relationship is easily seen.

**Scheme II**



from Ni(aryl)(R)(dmpe) is clearly facilitated by the addition of tertiary phosphine.[8]

Rearrangements of $\sigma$-aryls to $\pi$-arene complexes are, of course, known; those of chromium(III) having been extensively studied many years ago by H. H. Zeiss.[7] However, the reactions are not strightforward and may involve disproportionation and hydrogen abstractions. Further, the $\sigma$- to $\pi$-rearrangement on hydrolysis of a variety of $[Cr(aryl)_3(THF)_3]$ complexes after treatment with diethyl ether is said to be inhibited by ortho substituents; when the aryl = $2\text{-}MeC_6H_4$ or $2,6\text{-}Me_2C_6H_4$, little or no $\pi$-complex is obtained.[7c,9] Note also that $Cr(benzyl)_3(THF)_3$ is known to rearrange to $Cr(\eta^6\text{-toluene})(\eta^6\text{-2-benzyltoluene})$.[10]

Reductive coupling is also the dominant pathway in the reactions of isocyanides with **1** (eq iv, Scheme I). The colorless compounds **4** may result from the coupling discussed above, despite the nonformation of $\eta^6$-arene species. However, since reactions are known[11] where isocyanides displace $\pi$-complexed arenes, we examined the reactivity of **2** and **3** with excess *t*-BuNC in order to test whether such a complex could be an intermediate in reaction iii. Displacement of the $\pi$-arene ligand in **3** is facile and proceeds with retention of CO (eq iv, Scheme I); under the same conditions, the $PMe_3$ adduct **2** was inert as noted above. The greater lability of the arene in **3** is due, presumably, to the increased $\pi$-acceptor capability of CO versus $PMe_3$, which destabilizes the Os–arene interaction in **3** relative to **2**. Retention of the CO ligand in reaction iv might suggest that coordinatively saturated **3** undergoes

**Table IV. Fractional Atomic Coordinates (×10⁴) for $C_{37}H_{53}N_3Os$**

| | *x* | *y* | *z* |
|---|---|---|---|
| Os(1A) | 1139.3 (4) | 2381.5 (8) | 2851.0 (4) |
| Os(1B) | 6157.8 (4) | 2135.9 (6) | 2951.2 (4) |
| C(30A) | 1135 (8) | 1181 (14) | 3243 (9) |
| O(30A) | 1113 (6) | 309 (11) | 3465 (7) |
| C(1A) | 423 (9) | 2021 (13) | 2109 (9) |
| C(2A) | 1702 (9) | 1907 (14) | 2358 (10) |
| C(3A) | 1140 (12) | 3662 (20) | 2401 (13) |
| N(1A) | 12 (8) | 1871 (12) | 1651 (8) |
| N(2A) | 1981 (8) | 1667 (12) | 2033 (9) |
| N(3A) | 1130 (8) | 4385 (15) | 2123 (9) |
| C(4A) | −505 (10) | 1925 (16) | 1038 (11) |
| C(5A) | −435 (12) | 2874 (19) | 680 (13) |
| C(6A) | −524 (12) | 953 (20) | 650 (13) |
| C(7A) | −1096 (15) | 2033 (22) | 1263 (15) |
| C(8A) | 2193 (11) | 1366 (17) | 1485 (11) |
| C(9A) | 2283 (12) | 2385 (18) | 1153 (12) |
| C(10A) | 2802 (13) | 834 (19) | 1803 (13) |
| C(11A) | 1718 (12) | 711 (19) | 1030 (13) |
| C(12A) | 1121 (13) | 5334 (20) | 1716 (14) |
| C(13A) | 900 (17) | 5094 (26) | 985 (19) |
| C(14A) | 688 (20) | 6073 (31) | 1912 (20) |
| C(15A) | 1762 (19) | 5681 (28) | 1934 (19) |
| C(16A) | 510 (9) | 3022 (14) | 3283 (10) |
| C(17A) | 495 (9) | 2845 (14) | 3924 (10) |
| C(18A) | 51 (11) | 3238 (18) | 4201 (12) |
| C(19A) | −430 (12) | 3818 (18) | 3769 (13) |
| C(20A) | −438 (9) | 4031 (15) | 3123 (10) |
| C(21A) | 28 (9) | 3611 (15) | 2897 (10) |
| C(22A) | 961 (12) | 2191 (18) | 4441 (12) |
| C(23A) | 1859 (8) | 3045 (13) | 3639 (9) |
| C(24A) | 2409 (9) | 2584 (15) | 4017 (10) |
| C(25A) | 2819 (10) | 3097 (17) | 4529 (11) |
| C(26A) | 2741 (12) | 4093 (19) | 4695 (12) |
| C(27A) | 2196 (11) | 4577 (17) | 4345 (12) |
| C(28A) | 1762 (10) | 4059 (16) | 3827 (11) |
| C(29A) | 2558 (10) | 1507 (16) | 3868 (10) |
| O(30B) | 6092 (8) | 4195 (14) | 3551 (9) |
| C(30B) | 6124 (11) | 3438 (20) | 3342 (13) |
| C(1B) | 5499 (10) | 2493 (15) | 2192 (11) |
| C(2B) | 6699 (10) | 2595 (15) | 2503 (10) |
| C(3B) | 6166 (8) | 780 (13) | 2501 (9) |
| N(1B) | 5062 (9) | 2610 (12) | 1725 (9) |
| N(2B) | 7026 (9) | 2862 (12) | 2198 (9) |
| N(3B) | 6154 (8) | 55 (14) | 2217 (9) |
| C(4B) | 4549 (11) | 2562 (18) | 1112 (12) |
| C(5B) | 4446 (14) | 3604 (24) | 757 (15) |
| C(6B) | 4676 (21) | 1812 (34) | 673 (22) |
| C(7B) | 4000 (24) | 2270 (31) | 1317 (22) |
| C(8B) | 7253 (9) | 3204 (15) | 1682 (10) |
| C(9B) | 7272 (13) | 2234 (19) | 1250 (13) |
| C(10B) | 7908 (13) | 3658 (19) | 2003 (13) |

| | *x* | *y* | *z* | $U_{eq}$,[a] Å² |
|---|---|---|---|---|
| C(11B) | 6799 (11) | 3984 (18) | 1238 (12) | 89 (8) |
| C(12B) | 6129 (14) | −858 (22) | 1805 (15) | 107 (9) |
| C(13B) | 6009 (16) | −505 (25) | 1125 (18) | 157 (13) |
| C(14B) | 5626 (23) | −1532 (37) | 1974 (22) | 232 (20) |
| C(15B) | 6740 (19) | −1333 (29) | 2074 (18) | 177 (15) |
| C(16B) | 5507 (9) | 1488 (14) | 3364 (10) | 55 (6) |
| C(17B) | 5489 (10) | 1656 (16) | 4007 (11) | 68 (6) |
| C(18B) | 5005 (12) | 1236 (18) | 4211 (13) | 92 (8) |
| C(19B) | 4548 (13) | 678 (20) | 3775 (15) | 104 (9) |
| C(20B) | 4556 (11) | 485 (17) | 3143 (13) | 83 (7) |
| C(21B) | 5024 (10) | 898 (15) | 2942 (10) | 63 (6) |
| C(22B) | 5955 (10) | 2312 (16) | 4538 (11) | 75 (7) |
| C(23B) | 6851 (9) | 1492 (14) | 3769 (9) | 50 (5) |
| C(24B) | 7392 (10) | 1987 (16) | 4147 (11) | 65 (6) |
| C(25B) | 7826 (12) | 1505 (20) | 4682 (13) | 93 (8) |
| C(26B) | 7733 (12) | 494 (20) | 4816 (13) | 97 (8) |
| C(27B) | 7243 (11) | −52 (17) | 4465 (12) | 82 (7) |
| C(28B) | 6794 (10) | 465 (16) | 3937 (11) | 70 (7) |
| C(29B) | 7541 (11) | 3139 (19) | 4048 (12) | 92 (8) |

[a] $U_{eq}$ according to Hamilton (1959).

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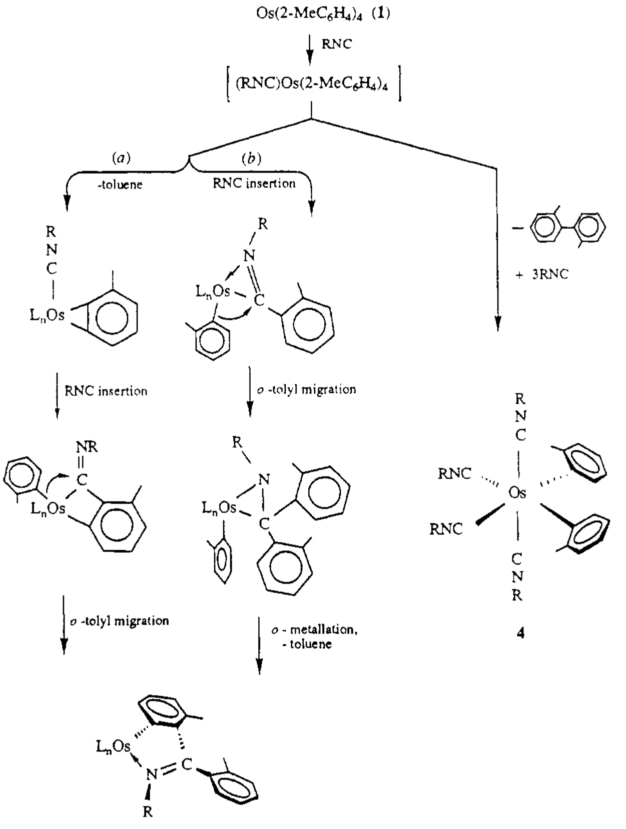
**Table V. Bond Lengths (Å) and Angles (deg) for $OsPC_{31}H_{37} \bullet Et_2O$**

| Bond Lengths | | | |
|---|---|---|---|
| P(1)-Os(1) | 2.316 (4) | C(11)-Os(1) | 2.162 (8) |
| C(21)-Os(1) | 2.140 (8) | C(31)-Os(1) | 2.222 (8) |
| C(32)-Os(1) | 2.291 (8) | C(33)-Os(1) | 2.238 (9) |
| C(34)-Os(1) | 2.258 (8) | C(35)-Os(1) | 2.328 (8) |
| C(36)-Os(1) | 2.346 (8) | C(1)-P(1) | 1.822 (9) |
| C(2)-P(1) | 1.803 (10) | C(3)-P(1) | 1.818 (10) |
| C(12)-C(11) | 1.405 (10) | C(16)-C(11) | 1.426 (9) |
| C(13)-C(12) | 1.388 (11) | C(14)-C(13) | 1.389 (12) |
| C(15)-C(14) | 1.339 (12) | C(16)-C(15) | 1.407 (11) |
| C(161)-C(16) | 1.524 (12) | C(22)-C(21) | 1.400 (9) |
| C(26)-C(21) | 1.419 (9) | C(23)C(22) | 1.380 (9) |
| C(24)-C(23) | 1.395 (11) | C(25)-C(24) | 1.392 (12) |
| C(26)-C(25) | 1.406 (10) | C(261)-C(26) | 1.509 (12) |
| C(32)-C(31) | 1.403 (10) | C(36)-C(31) | 1.426 (9) |
| C(33)-C(32) | 1.394 (10) | C(34)-C(33) | 1.409 (10) |
| C(35)-C(34) | 1.422 (11) | C(36)-C(35) | 1.408 (10) |
| C(351)-C(35) | 1.510 (11) | C(41)-C(36) | 1.507 (11) |
| C(41)-C(42) | 1.368 (10) | C(43)-C(42) | 1.395 (11) |
| C(421)-C(42) | 1.524 (12) | C(46)-C(41) | 1.391 (10) |
| C(44)-C(43) | 1.374 (12) | C(45)-C(44) | 1.380 (13) |
| C(46)-C(45) | 1.388 (12) | C(10)-O(1) | 1.495 (25) |
| C(30)-O(1) | 1.324 (22) | C(20)-C(10) | 1.218 (33) |
| C(40)-C(30) | 1.356 (29) | | |
| Bond Angles | | | |
| C(11)-Os(1)-P(1) | 81.3 (3) | C(21)-Os(1)-P(1) | 92.0 (3) |
| C(21)-Os(1)-C(11) | 90.6 (3) | C(31)-Os(1)-P(1) | 90.2 (3) |
| C(31)-Os(1)-C(11) | 134.2 (2) | C(31)-Os(1)-C(21) | 134.8 (2) |
| C(32)-Os(1)-P(1) | 105.9 (3) | C(32)-Os(1)-C(11) | 103.6 (3) |
| C(32)-Os(1)-C(21) | 158.5 (2) | C(32)-Os(1)-C(31) | 36.2 (2) |
| C(33)-Os(1)-P(1) | 138.7 (2) | C(33)-Os(1)-C(11) | 92.7 (3) |
| C(33)-Os(1)-C(21) | 129.0 (3) | C(33)-Os(1)-C(31) | 65.1 (3) |
| C(33)-Os(1)-C(32) | 35.8 (2) | C(34)-Os(1)-P(1) | 166.3 (2) |
| C(34)-Os(1)-C(11) | 110.0 (3) | C(34)-Os(1)-C(21) | 95.5 (3) |
| C(34)-Os(1)-C(31) | 76.4 (4) | C(34)-Os(1)-C(32) | 64.6 (4) |
| C(34)-Os(1)-C(33) | 36.5 (2) | C(35)-Os(1)-P(1) | 134.6 (2) |
| C(35)-Os(1)-C(11) | 143.6 (2) | C(35)-Os(1)-C(21) | 83.0 (3) |
| C(35)-Os(1)-C(31) | 64.3 (3) | C(35)-Os(1)-C(32) | 76.0 (3) |
| C(35)-Os(1)-C(33) | 65.2 (4) | C(35)-Os(1)-C(34) | 36.1 (2) |
| C(36)-Os(1)-P(1) | 103.3 (3) | C(36)-Os(1)-C(11) | 168.2 (2) |
| C(36)-Os(1)-C(21) | 100.0 (3) | C(36)-Os(1)-C(31) | 36.2 (2) |
| C(36)-Os(1)-C(32) | 64.8 (3) | C(36)-Os(1)-C(33) | 76.6 (3) |
| C(36)-Os(1)-C(34) | 64.2 (3) | C(36)-Os(1)-C(35) | 35.1 (2) |
| C(1)-P(1)-Os(1) | 114.9 (4) | C(2)-P(1)-Os(1) | 115.8 (4) |
| C(2)-P(1)-C(1) | 100.5 (5) | C(3)-P(1)-Os(1) | 121.1 (4) |
| C(3)-P(1)-C(1) | 99.5 (5) | C(3)-P(1)-C(2) | 101.7 (5) |
| C(12)-C(11)-Os(1) | 119.3 (5) | C(16)-C(11)-Os(1) | 126.9 (6) |
| C(16)-C(11)-C(12) | 113.7 (7) | C(13)-C(12)-C(11) | 125.4 (8) |
| C(14)-C(13)-C(12) | 118.1 (9) | C(15)-C(14)-C(13) | 119.5 (8) |
| C(16)-C(15)-C(14) | 123.0 (8) | C(15)-C(16)-C(11) | 120.3 (8) |
| C(161)-C(16)-C(11) | 125.4 (7) | C(161)-C(16)-C(15) | 114.3 (7) |
| C(22)-C(21)-Os(1) | 119.5 (5) | C(26)-C(21)-Os(1) | 124.2 (5) |
| C(26)-C(21)-C(22) | 115.1 (6) | C(23)-C(22)-C(21) | 125.3 (7) |
| C(24)-C(23)-C(22) | 118.7 (8) | C(25)-C(24)-C(23) | 118.5 (7) |
| C(26)-C(25)-C(24) | 122.1 (8) | C(25)-C(26)-C(21) | 120.2 (7) |
| C(261)-C(26)-C(21) | 124.0 (7) | C(261)-C(26)-C(25) | 115.8 (7) |
| C(32)-C(31)-Os(1) | 74.6 (5) | C(36)-C(31)-Os(1) | 76.6 (5) |
| C(36)-C(31)-C(32) | 122.8 (7) | C(31)-C(32)-Os(1) | 69.2 (4) |
| C(33)-C(32)-Os(1) | 70.0 (5) | C(33)-C(32)-C(31) | 118.1 (7) |
| C(32)-C(33)-Os(1) | 74.1 (5) | C(34)-C(33)-Os(1) | 72.5 (5) |
| C(34)-C(33)-C(32) | 120.3 (8) | C(33)-C(34)-Os(1) | 71.0 (5) |
| C(35)-C(34)-Os(1) | 74.7 (5) | C(35)-C(34)-C(33) | 120.9 (7) |
| C(34)-C(35)-Os(1) | 69.2 (5) | C(36)-C(35)-Os(1) | 73.2 (5) |
| C(36)-C(35)-C(34) | 119.6 (7) | C(351)-C(35)-Os(1) | 132.1 (5) |
| C(351)-C(35)-C(34) | 118.7 (8) | C(351)-C(35)-C(36) | 121.6 (8) |
| C(31)-C(36)-Os(1) | 67.1 (4) | C(35)-C(36)-Os(1) | 71.8 (5) |
| C(35)-C(36)-C(31) | 117.5 (7) | C(41)-C(36)-Os(1) | 138.8 (4) |
| C(41)-C(36)-C(31) | 118.6 (7) | C(41)-C(36)-C(35) | 123.4 (6) |
| C(43)-C(42)-C(41) | 119.8 (8) | C(421)-C(42)-C(41) | 121.9 (8) |
| C(421)-C(42)-C(43) | 118.2 (8) | C(42)-C(41)-C(36) | 120.0 (7) |
| C(46)-C(41)-C(36) | 121.1 (7) | C(46)-C(41)-C(42) | 118.9 (8) |
| C(44)-C(43)-C(42) | 121.3 (9) | C(45)-C(44)-C(43) | 119.1 (9) |
| C(46)-C(45)-C(44) | 119.6 (9) | C(45)-C(46)-C(41) | 121.1 (8) |
| C(30)-O(1)-C(10) | 113.1 (19) | C(20)-C(10)-O(1) | 117.2 (24) |
| C(42)-C(30)-O(1) | 125.4 (23) | | |

**Scheme III**



$\eta^6$- to $\eta^4$-ring slippage[12] prior to attack by isocyanide. Further "unzipping" of the arene occurs as two, then three, isocyanides are coordinated. In this way, one three-coordinate, six-electron ligand is replaced by a facial configuration of three unidentate, two-electron donor isocyanides. The possibility that **6** is derived from attack of isocyanide on a decomposition product of **3** in solution cannot be excluded, however.

Formation of the second, minor products **5** in reaction iii cannot be explained by a reductive elimination mechanism. Two different possibilities for synthesis of the 5-membered Os–imine portion of the molecule are given in Scheme III. In path a, decomposition of the initial isocyanide adduct occurs as already described for rhenium,[1] i.e., via ortho-hydrogen transfer and elimination of toluene. Insertion of isocyanide into the more electron-rich of the two metal–aryl bonds, followed by migration of an *o*-tolyl ligand gives the observed grouping. Insertion of unsaturated molecules into metal–aryne bonds[13] and migrations to coordinated isocyanides[14] are well-known. However, cases of reductive elimination competing with $\beta$-hydrogen abstraction are quite rare.[6a] Path b differs mainly in that the C–H activating step occurs after the *o*-tolyl ligand has migrated to the isocyanide carbon and is related to or-

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(12) See ref 5b, p 255, and: Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499 and references therein.

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(14) See ref 4a, p 259, and: Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720.

tho-metalation reactions common in metal–(arylphosphine) chemistry.[15]

**Table VI. Bond Lengths (Å) and Angles (deg) for $C_{41}H_{56}N_4Os$**

| bond Lengths | | | |
|---|---|---|---|
| N(1)–Os(1) | 2.193 (24) | C(1)–Os(1) | 2.077 (20) |
| C(41)–Os(1) | 2.148 (39) | C(21)–Os(1) | 1.985 (23) |
| C(31)–Os(1) | 1.797 (36) | C(51)–Os(1) | 1.879 (40) |
| C(11)–N(1) | 1.529 (38) | C(15)–N(1) | 1.300 (20) |
| C(12)–C(11) | 1.545 (40) | C(13)–C(11) | 1.495 (46) |
| C(14)–C(11) | 1.494 (36) | C(2)–C(15) | 1.466 (41) |
| C(1A)–C(15) | 1.425 (39) | C(2)–C(1) | 1.442 (37) |
| C(6)–C(1) | 1.405 (43) | C(3)–C(2) | 1.448 (25) |
| C(4)–C(3) | 1.427 (48) | C(7)–C(3) | 1.571 (37) |
| C(5)–C(4) | 1.319 (46) | C(6)–C(5) | 1.397 (29) |
| C(2A)–C(1A) | 1.401 (43) | C(6A)–C(1A) | 1.302 (68) |
| C(3A)–C(2A) | 1.497 (41) | C(4A)–C(3A) | 1.290 (72) |
| C(5A)–C(4A) | 1.317 (59) | C(6A)–C(5A) | 1.455 (54) |
| C(7A)–C(6A) | 1.423 (60) | C(42)–C(41) | 1.468 (38) |
| C(46)–C(41) | 1.354 (49) | C(43)–C(42) | 1.411 (62) |
| C(47)–C(42) | 1.518 (50) | C(44)–C(43) | 1.279 (58) |
| C(45)–C(44) | 1.337 (44) | C(46)–C(45) | 1.406 (57) |
| N(2)–C(21) | 1.184 (23) | C(22)–N(2) | 1.454 (26) |
| C(23)–C(22) | 1.546 (45) | C(24)–C(22) | 1.490 (71) |
| C(25)–C(22) | 1.281 (58) | N(3)–C(31) | 1.217 (47) |
| C(32)–N(3) | 1.458 (77) | C(33)–C(32) | 1.533 (40) |
| C(34)–C(32) | 1.512 (86) | C(35)–C(32) | 1.676 (70) |
| C(35)–C(33) | 1.914 (85) | N(5)–C(51) | 1.193 (44) |
| C(52)–N(5) | 1.475 (72) | C(53)–C(52) | 1.344 (81) |
| C(54)–C(52) | 1.442 (43) | C(55)–C(52) | 1.411 (50) |
| Bond Angles | | | |
| C(1)–Os(1)–N(1) | 76.4 (10) | C(41)–Os(1)–N(1) | 89.1 (11) |
| C(41)–Os(1)–C(1) | 89.1 (11) | C(21)–Os(1)–N(1) | 100.7 (10) |
| C(21)–Os(1)–C(1) | 177.1 (14) | C(21)–Os(1)–C(41) | 90.2 (13) |
| C(31)–Os(1)–N(1) | 169.4 (8) | C(31)–Os(1)–C(1) | 94.0 (12) |
| C(31)–Os(1)–C(41) | 95.4 (15) | C(31)–Os(1)–C(21) | 88.9 (12) |
| C(51)–Os(1)–N(1) | 86.1 (12) | C(51)–Os(1)–C(1) | 82.8 (12) |
| C(51)–Os(1)–C(41) | 171.3 (8) | C(51)–Os(1)–C(21) | 97.8 (13) |
| C(51)–Os(1)–C(31) | 88.2 (17) | C(11)–N(1)–Os(1) | 120.8 (12) |
| C(15)–N(1)–Os(1) | 115.5 (18) | C(15)–N(1)–C(11) | 123.4 (21) |
| C(12)–C(11)–N(1) | 104.3 (28) | C(13)–C(11)–N(1) | 119.3 (17) |
| C(13)–C(11)–C(12) | 106.4 (24) | C(14)–C(11)–N(1) | 109.5 (20) |
| C(14)–C(11)–C(12) | 111.1 (18) | C(14)–C(11)–C(13) | 106.2 (31) |
| C(2)–C(15)–N(1) | 116.2 (22) | C(1A)–C(15)–N(1) | 126.7 (26) |
| C(1A)–C(15)–C(2) | 117.2 (20) | C(2)–C(1)–Os(1) | 114.9 (19) |
| C(6)–C(1)–Os(1) | 125.6 (23) | C(6)–C(1)–C(2) | 119.1 (20) |
| C(1)–C(2)–C(15) | 114.6 (18) | C(3)–C(2)–C(15) | 127.9 (23) |
| C(3)–C(2)–C(1) | 117.5 (24) | C(4)–C(3)–C(2) | 118.7 (23) |
| C(7)–C(3)–C(22) | 122.9 (25) | C(7)–C(3)–C(4) | 118.4 (19) |
| C(5)–C(4)–C(3) | 122.6 (21) | C(6)–C(5)–C(4) | 120.4 (30) |
| C(5)–C(6)–C(1) | 121.4 (26) | C(2A)–C(1A)–C(15) | 116.1 (34) |
| C(6A)–C(1A)–C(15) | 129.3 (36) | C(6A)–C(1A)–C(2A) | 114.5 (33) |
| C(3A)–C(2A)–C(1A) | 119.9 (41) | C(4A)–C(3A)–C(2A) | 112.7 (38) |
| C(5A)–C(4A)–C(3A) | 134.8 (37) | C(6A)–C(5A)–C(4A) | 106.5 (46) |
| C(5A)–C(6A)–C(1A) | 130.8 (42) | C(7A)–C(6A)–C(1A) | 125.7 (40) |
| C(7A)–C(6A)–C(5A) | 103.5 (45) | C(42)–C(41)–Os(1) | 128.5 (26) |
| C(46)–C(41)–Os(1) | 120.3 (22) | C(46)–C(41)–C(42) | 111.1 (35) |
| C(43)–C(42)–C(41) | 120.0 (34) | C(47)–C(42)–C(41) | 121.6 (36) |
| C(47)–C(42)–C(43) | 118.4 (28) | C(44)–C(43)–C(42) | 124.1 (32) |
| C(45)–C(44)–C(43) | 118.2 (48) | C(46)–C(45)–C(44) | 120.9 (39) |
| C(45)–C(46)–C(41) | 125.3 (28) | N(2)–C(21)–Os(1) | 169.3 (31) |
| C(22)–N(2)–C(21) | 172.1 (32) | C(23)–C(22)–N(2) | 112.8 (22) |
| C(24)–C(22)–N(2) | 106.2 (38) | C(24)–C(22)–C(23) | 108.0 (37) |
| C(25)–C(22)–N(2) | 109.6 (37) | C(25)–C(22)–C(23) | 117.0 (40) |
| C(25)–C(22)–C(24) | 102.2 (31) | N(3)–C(31)–Os(1) | 175.3 (29) |
| C(32)–N(3)–C(31) | 154.4 (42) | C(33)–C(32)–N(3) | 120.1 (46) |
| C(34)–C(32)–N(3) | 124.1 (54) | C(34)–C(32)–C(33) | 115.6 (67) |
| C(35)–C(32)–N(3) | 106.8 (55) | C(35)–C(32)–C(33) | 73.1 (34) |
| C(35)–C(32)–C(34) | 84.3 (49) | C(35)–C(33)–C(32) | 56.9 (27) |
| C(33)–C(35)–C(32) | 50.0 (25) | N(5)–C(51)–Os(1) | 175.0 (19) |
| C(52)–N(5)–C(51) | 154.3 (31) | C(53)–C(52)–N(5) | 105.2 (41) |
| C(54)–C(52)–N(5) | 107.6 (46) | C(54)–C(52)–C(53) | 117.3 (48) |
| C(55)–C(52)–N(5) | 105.5 (47) | C(55)–C(52)–C(53) | 115.8 (67) |
| C(55)–C(52)–C(54) | 104.6 (33) | | |

## Experimental Section

Reactions were performed under argon by using dry, oxygen-free solvents. Microanalyses were by Pascher or Imperial College Laboratories. Spectrometers: IR, Perkin-Elmer 1720 (Nujol mulls, values in cm$^{-1}$); NMR, Bruker WM-250, Perkin-Elmer R-24B, JEOL GSX 270 or FX 90Q (data in ppm relative to $SiMe_4$ ($^1H$, $^{13}C$) or 85% $H_3PO_4$ ($^{31}P$)); mass, VG 7070 (data refer to the ion due to $^{192}Os$; the expected isotope envelopes were observed). Melting points were determined in sealed capillaries under argon and are uncorrected.

**$Os[\eta^6\text{-}2\text{-}(2\text{-}MeC_6H_4)MeC_6H_4](2\text{-}MeC_6H_4)_2(PMe_3)$ (2).** A solution of 1 (0.30 g, 0.54 mmol) and $PMe_3$ (0.4 cm$^3$, 4 mmol) in hexane (30 cm$^3$) was stirred for 20 min. After removal of volatiles under reduced pressure, the yellow residue was extracted into diethyl ether (20 cm$^3$) which was filtered, concentrated (to ca. 10 cm$^3$), and held at −15 °C overnight to yield 0.36 g (94%) of yellow crystals (mp 215–219 °C dec) of the title complex as the monoetherate. Recrystallization from benzene–hexane gave the ether-free complex. Anal. Calcd for $C_{31}H_{37}POs$: C, 59.0; P, 4.9. Found: C, 58.9; P, 4.9. IR: 3065 w, 3028 m, 1602 w, 1573 m, 1366 s, 1300 m, 1281 m, 1012 m, 1001 m, 955 s, 936 m, 833 m, 767 s, 742 s, 736 sh, 676 m, 460 w. $^1H$ NMR (toluene-$d_8$, −60 °C, 250 MHz): 0.95 (d, $J_{PH}$ = 9 Hz, 9 H, $PMe_3$), 1.20, 1.99, 2.34, 2.46 (all s, 3 H each, 2-*Me*$C_6H_4$) 4.53 (t, $J$ = 6 Hz, 1 H), 4.61 (d, $J$ = 6 Hz, 1 H), 4.63 (d, $J$ = 6 Hz, 1 H), 5.39 (t, $J$ = 6 Hz, 1 H), 6.8–7.4 (m, 10 H), 7.8–8.0 (m, 2 H). $^{31}P\{^1H\}$ NMR (toluene-$d_8$, −60 °C, 36.3 MHz): −47.1 (s). MS (EI, 70 eV): 182 ($C_{14}H_{14}$), 167 ($C_{13}H_{11}$).

**Reaction of 2 with Benzene.** A solution of 2 (0.05 g, 0.08 mmol) in benzene (5 cm$^3$) was warmed to 100 °C for 1 h. After being cooled to room temperature, the solution was concentrated to 2 cm$^3$ and hexane (2 cm$^3$) was added. Bright yellow crystals of $Os(\eta^6\text{-}C_6H_6)(2\text{-}MeC_6H_4)_2(PMe_3)$ (0.03 g, 70%) were collected after 2 h. The compound darkens above 85 °C but does not appear to melt below 300 °C. Anal. Calcd for $C_{23}H_{29}POs$: C, 52.5; H, 5.6. Found: C, 52.6; H, 5.6. IR: 1572 m, 1304 w, 1279 w, 1139 w, 1015 m, 957 s, 939 s, 855 w, 801 m, 750 s, 742 s, 724 m, 676 w, 638 w, 620 m, 374 w, 338 w. $^1H$ NMR (chloroform-$d$, 27 °C, 270 MHz): 1.32 (d, $J_{PH}$ = 9 Hz, 9 H, $PMe_3$), 2.32 (s, 6 H, 2-*Me*$C_6H_4$), 5.24 (d, $J_{PH}$ = 0.7 Hz, 6 H, $C_6H_6$), 6.57, 6.82, 7.02, 7.43 (all m, 2 H each, 2-$MeC_6$*$H_4$*). $^{31}P\{^1H\}$ NMR (chloroform-$d$, 27 °C, 36.3 MHz): −44.5 (s).

**$Os[\eta^6\text{-}2\text{-}(2\text{-}MeC_6H_4)MeC_6H_4](2\text{-}MeC_6H_4)_2(CO)$ (3).** Carbon monoxide (5 cm$^3$, 0.2 mmol) was syringed into a flask containing 1 (0.10 g, 0.18 mmol) in hexane (20 cm$^3$) sealed with a rubber septum. The maroon solution slowly deposited a yellow microcrystalline precipitate which was collected by filtration after 1 h: yield 0.09 g, 85%; mp 100–101 °C. Anal. Calcd for $C_{29}H_{28}OOs$: C, 59.7; H, 4.8. Found: C, 59.1; H, 4.8. IR: 3076 w, 1917 s, 1575 m, 1555 w, 1403 w, 1163 m, 1064 w, 1009 m, 835 m, 761 s, 741 s, 727 m, 601 m, 575 m, 562 m, 546 m, 455 w. $^1H$ NMR (benzene-$d_6$, 20 °C, 250 MHz): 1.75, 1.76, 2.33, 2.60 (all s, 3 H each, 2-*Me*$C_6H_4$), 4.74 (d, $J$ = 6 Hz, 1 H), 4.94 (t, $J$ = 6 Hz, 1 H), 5.05 (t, $J$ = 6 Hz, 1 H), 5.31 (d, $J$ = 6 Hz, 1 H), 6.8–7.3 (m, 9 H), 7.52 (t, $J$ = 7 Hz, 2 H), 7.97 (d, $J$ = 7 Hz, 1 H).

**Reaction of 1 with *t*-BuNC.** Neat *t*-BuNC (0.15 cm$^3$, 1.5 mmol) was added to a stirred solution of 1 (0.18 g, 0.32 mmol) in hexane (30 cm$^3$). The yellow-orange solution was evaporated in vacuo and the residue extracted with hexane (10 cm$^3$), filtration, concentration, and cooling of which gave orange blocks of **5a** (0.05 g, 19%; mp 93–96 °C) contaminated with a small amount of 4 (ca. 0.01 g). More of the latter compound was obtained by extracting the residue from the above reaction with diethyl ether (10 cm$^3$); concentration and cooling gave colorless crystals in 57% combined yield (0.13 g, mp 189–190 °C). ***cis*-$Os(2\text{-}MeC_6H_4)_2(t\text{-}BuNC)_4$ (4a).** Anal. Calcd for $C_{34}H_{50}N_4Os$: C, 58.0; H, 7.1; N, 7.9. Found: C, 57.9; H, 7.1; N, 7.9. IR: 2172 w, 2105 s, 2050 s br, 1570 m, 1550 w, 1367 m, 1232 w, 1207 s, 1011 w, 747 sh, 737 s, 560 m, 548 m, 439 m. $^1H$ NMR (chloroform-$d$, 20 °C, 270 MHz): 1.42 (s, 18 H, *t*-Bu), 1.45 (s, 18 H, *t*-Bu), 6.54 (td, $J$ = 7 Hz, 2 Hz, 2 H), 6.74 (td, $J$ = 7 Hz, 2 H), 6.89 (dd, $J$ = 7 Hz, 2 Hz, 2 H),

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[15] See ref 5a, p 1219, and for an example: Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448.

**Table VII. Bond Lengths (Å) and Angles (deg) for $C_{37}H_{53}N_3Os$**

| | molecule 1 (n = A) | molecule 2 (n = B) | | molecule 1 (n = A) | molecule 2 (n = B) |
|---|---|---|---|---|---|
| Bond Lengths | | | | | |
| C(1n)–Os(1n) | 1.968 (18) | 1.913 (21) | C(11n)–C(8n) | 1.496 (33) | 1.562 (31) |
| C(2n)–Os(1n) | 2.027 (25) | 1.912 (27) | C(13n)–C(12n) | 1.523 (49) | 1.470 (50) |
| C(3n)–Os(1n) | 1.937 (29) | 2.027 (20) | C(14n)–C(12n) | 1.551 (58) | 1.601 (67) |
| C(16n)–Os(1n) | 2.142 (25) | 2.149 (19) | C(15n)–C(12n) | 1.491 (52) | 1.495 (51) |
| C(23n)–Os(1n) | 2.156 (18) | 2.160 (25) | C(17n)–C(16n) | 1.407 (32) | 1.412 (34) |
| C(30n)–Os(1n) | 1.786 (20) | 1.102 (34) | C(18n)–C(17n) | 1.441 (38) | 1.444 (41) |
| O(30n)–C(30n) | 1.246 (24) | 1.915 (29) | C(19n)–C(18n) | 1.429 (33) | 1.385 (36) |
| N(1n)–C(1n) | 1.153 (23) | 1.193 (26) | C(20n)–C(19n) | 1.410 (37) | 1.385 (44) |
| N(2n)–C(2n) | 1.139 (32) | 1.203 (34) | C(21n)–C(16n) | 1.399 (27) | 1.429 (27) |
| N(3n)–C(3n) | 1.117 (34) | 1.124 (27) | C(22n)–C(17n) | 1.546 (31) | 1.405 (38) |
| C(4n)–N(1n) | 1.481 (25) | 1.474 (28) | C(21n)–C(20n) | 1.433 (35) | 1.563 (30) |
| C(8n)–N(2n) | 1.468 (35) | 1.442 (33) | C(24n)–C(23n) | 1.419 (26) | 1.424 (28) |
| C(12n)–N(3n) | 1.516 (36) | 1.479 (36) | C(25n)–C(24n) | 1.383 (28) | 1.418 (31) |
| C(5n)–C(4n) | 1.498 (36) | 1.546 (41) | C(26n)–C(25n) | 1.381 (35) | 1.389 (39) |
| C(6n)–C(4n) | 1.516 (37) | 1.456 (56) | C(28n)–C(23n) | 1.427 (29) | 1.358 (35) |
| C(7n)–C(4n) | 1.606 (47) | 1.529 (68) | C(27n)–C(26n) | 1.408 (34) | 1.411 (29) |
| C(9n)–C(8n) | 1.558 (37) | 1.583 (35) | C(27n)–C(28n) | 1.419 (30) | 1.579 (35) |
| C(10n)–C(8n) | 1.537 (36) | 1.583 (35) | C(29n)–C(24n) | 1.513 (31) | 1.447 (31) |
| Bond Angles | | | | | |
| C(1n)–Os(1n)–C(30n) | 92.2 (8) | 91.3 (10) | C(10n)–C(8n)–C(9n) | 110.7 (22) | 110.8 (21) |
| C(2n)–Os(1n)–C(30n) | 94.4 (10) | 93.7 (12) | C(11n)–C(8n)–N(2n) | 108.0 (23) | 109.3 (20) |
| C(2n)–Os(1n)–C(1n) | 91.6 (9) | 88.6 (11) | C(11n)–C(8n)–C(9n) | 111.9 (20) | 107.9 (18) |
| C(3n)–Os(1n)–C(30n) | 178.2 (10) | 177.5 (8) | C(11n)–C(8n)–C(10n) | 114.9 (21) | 113.3 (19) |
| C(3n)–Os(1n)–C(1n) | 86.5 (10) | 86.2 (9) | C(13n)–C(12n)–N(3n) | 111.3 (23) | 107.3 (24) |
| C(3n)–Os(1n)–C(2n) | 84.5 (11) | 86.0 (9) | C(14n)–C(12n)–N(3n) | 104.4 (28) | 101.8 (30) |
| C(16n)–Os(1n)–C(30n) | 92.0 (10) | 92.3 (11) | C(14n)–C(12n)–C(13n) | 111.7 (26) | 118.4 (28) |
| C(16n)–Os(1n)–C(1n) | 85.4 (9) | 88.0 (10) | C(15n)–C(12n)–N(3n) | 103.9 (23) | 104.6 (24) |
| C(16n)–Os(1n)–C(2n) | 173.1 (7) | 173.2 (8) | C(15n)–C(12n)–C(13n) | 111.5 (33) | 112.0 (34) |
| C(16n)–Os(1n)–C(3n) | 89.1 (11) | 87.9 (9) | C(15n)–C(12n)–C(14n) | 113.6 (28) | 111.2 (30) |
| C(23n)–Os(1n)–C(30n) | 96.1 (8) | 96.7 (9) | C(17n)–C(16n)–Os(1n) | 126.2 (15) | 125.5 (15) |
| C(23n)–Os(1n)–C(1n) | 169.9 (7) | 171.0 (8) | C(21n)–C(16n)–Os(1n) | 119.5 (17) | 118.0 (17) |
| C(23n)–Os(1n)–C(2n) | 93.5 (8) | 95.0 (9) | C(21n)–C(16n)–C(17n) | 114.0 (21) | 116.3 (22) |
| C(23n)–Os(1n)–C(3n) | 85.3 (9) | 85.8 (8) | C(18n)–C(17n)–C(16n) | 125.9 (19) | 120.3 (20) |
| C(23n)–Os(1n)–C(16n) | 88.5 (8) | 87.5 (8) | C(22n)–C(17n)–C(16n) | 124.4 (22) | 124.7 (22) |
| O(30n)–C(30n)–Os(1n) | 174.8 (15) | 177.9 (20) | C(22n)–C(17n)–C(18n) | 109.7 (21) | 114.9 (22) |
| N(1n)–C(1n)–Os(1n) | 175.0 (17) | 172.6 (19) | C(19n)–C(18n)–C(17n) | 116.3 (24) | 120.4 (27) |
| N(2n)–C(2n)–Os(1n) | 174.1 (15) | 177.2 (17) | C(20n)–C(19n)–C(18n) | 120.4 (26) | 120.8 (30) |
| N(3n)–C(3n)–Os(1n) | 177.8 (22) | 175.9 (16) | C(21n)–C(20n)–C(19n) | 118.8 (19) | 118.9 (22) |
| C(4n)–N(1n)–C(1n) | 167.3 (18) | 169.3 (20) | C(20n)–C(21n)–C(16n) | 124.4 (21) | 123.2 (22) |
| C(8n)–N(2n)–C(2n) | 165.6 (18) | 163.3 (18) | C(24n)–C(23n)–Os(1n) | 128.1 (14) | 126.2 (15) |
| C(12n)–N(3n)–C(3n) | 176.9 (26) | 176.3 (22) | C(28n)–C(23n)–Os(1n) | 116.4 (13) | 118.4 (14) |
| C(5n)–C(4n)–N(1n) | 107.7 (18) | 111.0 (20) | C(28n)–C(23n)–C(24n) | 115.5 (16) | 115.3 (17) |
| C(6n)–C(4n)–N(1n) | 108.8 (1) | 109.3 (25) | C(25n)–C(24n)–C(23n) | 121.4 (19) | 122.5 (21) |
| C(6n)–C(4n)–C(5n) | 114.0 (23) | 108.1 (29) | C(29n)–C(24n)–C(23n) | 120.2 (17) | 123.6 (18) |
| C(7n)–C(4n)–N(1n) | 105.9 (20) | 105.9 (25) | C(29n)–C(2jn)–C(25n) | 118.3 (18) | 133.8 (19) |
| C(7n)–C(4n)–C(5n) | 108.9 (21) | 110.4 (27) | C(26n)–C(25n)–Cn24n) | 123.4 (20) | 118.3 (22) |
| C(7n)–C(4n)–C(6n) | 111.2 (21) | 112.2 (30) | C(27n)–C(26n)–C(25n) | 117.3 (21) | 123.2 (23) |
| C(9n)–C(8n)–N(2n) | 105.2 (19) | 106.6 (19) | C(28n)–C(27n)–C(26n) | 120.2 (22) | 117.6 (22) |
| C(10n)–C(8n)–N(2n) | 105.3 (19) | 108.7 (18) | C(27n)–C(28n)–C(23n) | 122.1 (19) | 122.9 (19) |

7.50 (dd, *J* = 7 Hz, 2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (chloroform-*d*, 20 °C, 69.7 MHz): 29.23 (s, 2-*Me*$C_6H_4$), 30.96 (s, C*Me*$_3$), 31.66 (s, C*Me*$_3$), 55.27 (s, *C*Me$_3$) 55.54 (s, *C*Me$_3$), 120.2, 122.9, 126.5, 147.4, 147.9, 154.5 (2-Me*C*$_6$H$_4$), 140.6 (*C*N), 141.0 (*C*N). MS (EI, 70 eV): 706 (M$^+$), 615 (M$^+$ – $C_7H_7$, 532 (M$^+$ – $C_7H_7$ – *t*-BuNC). ***fac*-Os{*C*,*N*-3-Me[2-C(2-MeC$_6$H$_4$)NCMe$_3$]C$_6$H$_3$}(2-MeC$_6$H$_4$)(*t*-BuNC)$_3$ (5a).** Anal. Calcd for $C_{41}H_{56}N_4Os$: C, 61.9; H, 7.1; N, 7.1. Found: C, 62.5; H, 7.2; N, 7.1. MS (EI, 70 eV): 713 (M$^+$ – *t*-BuNC), 630 (M$^+$ – 2*t*-BuNC). IR: 3021 m, 2129 s, 2039 s br, 1570 m, 1547 m, 1516 w, 1366 s, 1230 m, 1213 s, 1188 s, 1157 m, 1012 m, 769 s, 737 s, 445 m.

**Reaction of 1 with Xylyl Isocyanide.** The above procedure was repeated using solid 2,6-$Me_2C_6H_3NC$ (0.27 g, 2.2 mmol) and 1 (0.30 g, 0.54 mmol). ***cis*-Os(2-MeC$_6$H$_4$)$_2$[CN(2,6-Me$_2$C$_6$H$_3$)]$_4$ (4b)**: yield 0.20 g (41%); colorless plates; mp 164–165 °C. Anal. Calcd for $C_{50}H_{50}N_4Os$: 66.9; H, 5.6; N, 6.2. Found: C, 66.7; H, 5.6; N, 6.1. IR: 2158 m, 2090 s, 2048 s br, 2001 sh, 1588 w, 1573 w, 1261 m, 1092 m, 1012 m, 804 m, 775 s, 741 s, 721 m, 659 m, 494 m. $^1H$ NMR (chloroform-*d*, 270 MHz, 21 °C): 2.34 (s, 24 H, 2,6-*Me*$_2$C$_6$H$_3$), 2.49 (s, 6 H, 2-*Me*C$_6$H$_4$), 6.63 (td, *J* = 7 Hz, 1 Hz, 2 H), 6.81 (td, *J* = 7 Hz, 1 Hz, 2 H), 6.9–7.1 (m, 14 H), 7.91 (dd, *J* = 7 Hz, 1 Hz, 2 H). $^{13}C\{^1H\}$ NMR (chloroform-*d*, 69.7 MHz, 21 °C): 19.04 (2,6-*Me*$_2$C$_6$H$_3$), 30.57 (2-*Me*C$_6$H$_4$), 121.4, 123.5, 126.7, 147.5, 148.3, 151.1 (2-Me*C*$_6$H$_4$), 127.3, 127.4, 127.7, 127.8, 128.7, 129.8, 134.4, 135.2, (2,6-Me$_2$*C*$_6$H$_3$), 149.2, 152.4 (*CN*). **fac-Os-{(*C*,*N*-3-Me)2-C(2-MeC$_6$H$_4$)NC(2,6-Me$_2$C$_6$H$_3$)C$_6$H$_3$}(2-MeC$_6$H$_4$)[CN(2,6-Me$_2$C$_6$H$_3$)]$_3$ (5b)**: yield 0.11 g (19%), orange plates; mp 210–214 °C. Anal. Calcd for $C_{57}H_{56}N_4Os$: C, 69.3; H, 5.7; N, 5.7. Found: C, 69.3; H, 5.7; N, 5.7. IR: 2117 s, 2034 s, 2009 s, 1591 m, 1568 m, 1548 m, 1505 w, 1313 m, 1165 m, 1095 w, 771 s, 735 m, 731 w, 723 w, 682 w, 503 m. MS (FAB, ONPOE): 989 (MH$^+$, 2%), 897 (MH$^+$ – $C_7H_7$, 5%).

**Os(2-MeC$_6$H$_4$)$_2$(*t*-BuNC)$_3$(CO) (6).** Excess *t*-BuNC (ca. 0.1 cm$^3$) was added to a stirred suspension of **3** (0.10 g, 0.17 mmol) in hexane (20 cm$^3$). After 2 h, microcrystals of the product were filtered off: yield 72% (0.08 g); mp 166–167 °C. Recrystallization from diethyl ether/hexane gave large colorless plates suitable for X-ray diffraction. Anal. Calcd for $C_{30}H_{41}N_3OOs$: C, 55.4; H, 6.4; N, 6.5. Found: C, 55.7; H, 6.4, N, 6.4. IR: 3036 w, 2194 s, 2144 s, 2102 s, 1949 s, 1574 m, 1232 w, 1206 s, 1015 m, 737 s, 723 sh, 608 s, 544 w, 514 w, 436 m. $^1H$ NMR (chloroform-*d*, 270 MHz, 22 °C): 1.50 (s, 9 H, *t*-Bu), 1.52 (s, 18 H, *t*-Bu), 2.33 (s, 6 H, 2-*Me*C$_6$H$_4$), 6.64 (td, *J* = 7 Hz, 1 Hz, 2 H), 6.83 (td, *J* = 7 Hz, 1 Hz, 2 H), 6.69 (dd, *J* = 7 Hz, 1 Hz, 2 H), 7.52 (dd, *J* = 7 Hz, 1 Hz, 2 H). $^{13}C\{^1H\}$ NMR (chloroform-*d*, 69.7 MHz, 22 °C): 29.28 (2-*Me*C$_6$H$_4$), 30.45, 31.21 (C*Me*$_3$), 56.20, 56.58 (*C*Me$_3$), 121.3, 123.5, 127.3, 146.5, 147.6, 149.1 (2-$MeC_6H_4$), 132.2, 135.1 (CN), 186.4 (CO). MS (EI, 70 eV): 651 ($M^+$, 8%), 623 ($M^+ - CO$, 7%), 559 ($M^+ - C_7H_8$).

**X-ray Crystal Structure Determinations.** Crystals of the three compounds were sealed under argon in thin-walled glass capillaries. All X-ray measurements were made by using an Enraf-Nonius CAD4 with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å), operating in the $\omega/2\theta$ scan mode, following previously detailed procedures.[1b]

The structures were solved via application of the heavy-atom method and refined by full-matrix least-squares procedures. For structures **2** and **5a**, non-hydrogen atoms were refined with anisotropic displacement factors; hydrogen atoms were inserted in idealized positions and allowed to ride on the parent carbon atom with refined group $U_{iso}$ values (**2**) or fixed $U_{iso}$ values (**5a**). For structure **6**, a very strong *a*-glide pseudosymmetry (the correct space group was $P2_1/c$) caused serious correlation problems. As a result, only the Os atom was refined anistropically; all the lighter atoms were refined isotropically and no hydrogens were included. For both **5a** and **6**, severe torsional disorder in the *tert*-butyl groups also caused problems in the refinement. However, in each case it was possible to represent each $Me_3C$ group by four atoms only. Details of the data collections and refinements are given in Table I. Atomic positional parameters are given in Tables II–IV; selected bond distances and angles in Tables V–VII.

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**Registry No.** **1**, 101191-32-6; **2**, 120022-42-6; **3**, 120022-43-7; **4a**, 120022-44-8; **4b**, 120022-48-2; **5b**, 120022-49-3; **6**, 120022-46-0; Os($\eta^6$-$C_6H_6$) (2-$MeC_6H_4$)$_2$ ($PMe_3$), 120022-47-1; 2,6-$Me_2C_6H_3NC$, 2769-71-3.

**Supplementary Material Available:** Tables of $U_{ij}$ values and full lists of bond lengths and angles (8 pages); listings of $F_o/F_c$ values (83 pages). Ordering information is given on any current masthead page.

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# *Communications*

## Polysilyl Complexes of Platinum—Synthesis and Thermochemistry

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*Summary:* The reaction of LiSiR($SiMe_3$)$_2$ (R = $SiMe_3$ or Ph) with (dcpe)$PtCl_2$ [dcpe = bis(dicyclohexylphosphino)ethane] affords two stable polysilyl derivatives of $d^8$ platinum, (dcpe)Pt[SiR($SiMe_3$)$_2$]Cl. These compounds undergo a thermal isomerization involving a trimethylsilyl–chlorine interchange across the platinum–silicon bond. The mechanism of this isomerization is considered.

Platinum complexes have been reported to catalyze a number of polysilane-forming reactions including the dehydrogenative coupling of monomeric polyhydridosilanes[1] and the redistribution reaction of hydridodisilanes.[2] Little is known about the mechanism of these reactions; however, polysilylplatinum species seem likely candidates for chain-growing intermediates in these processes.[3] Despite their potential mechanistic significance, only one well-characterized example of a polysilylplatinum complex is known.[4,5] We therefore describe the synthesis and properties of two stable polysilyl derivatives of $d^8$ platinum and their novel thermal isomerizations.

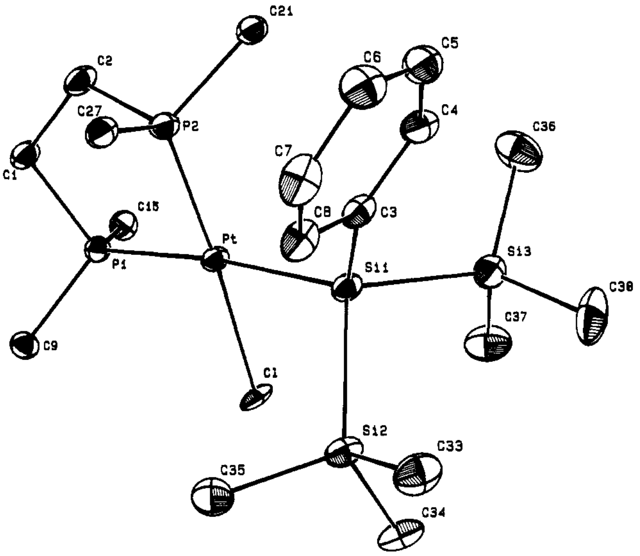

**Figure 1.** ORTEP diagram of (dcpe)Pt[SiPh($SiMe_3$)$_2$]Cl (**1b**) showing non-hydrogen atoms. The nonpendant carbons of the cyclohexane rings have been removed for clarity. Thermal ellipsoids are at 30% probability level. Selected bond distances (Å) and angles (deg): Pt–Cl, 2.408 (1); Pt–Si1, 2.423 (2); Pt–P1, 2.326 (2); Pt–P2, 2.220 (2); Si1–Si2, 2.378 (3); Si1–Si3, 2.373 (3); Si1–C3, 1.925 (7); Cl–Pt–P1, 88.56 (6); Cl–Pt–Si1, 86.50 (6); P2–Pt–P1, 87.03 (6); P2–Pt–Si1, 97.85 (6); Si1–Si2–Si3, 105.2 (1).

Polysilylplatinum complexes **1a** and **1b** have been pre-

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