Isocyanide-Mediated C–H Activation, C–C Coupling, and Transformation of a Bis(diphenylphosphino)methane Ligand in Triosmium Clusters

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Thermolysis of $Os_3(CO)_9(CNR)(\mu\text{-dppm})$ (1), prepared by reactions of $Os_3(CO)_{10}(CNR)(NCMe)$ with bis(diphenylphosphino)methane (dppm) in refluxing toluene, yields the unprecedented complexes $(\mu\text{-H})_2Os_3(CO)_7(CNR)\{Ph_2PCHP(Ph)C_6H_4\}$ (2). Two kinds of C–H activations, including ortho metalation of a phenyl group as well as the unusual activation of the methylene group of the dppm ligand, have been observed in these transformations. An intermediate has been isolated and identified with the proposed formulation of $(\mu\text{-H})Os_3(CO)_8(CNPr)\{Ph_2PCH_2P(Ph)C_6H_4\}$. In the presence of PPh_3, pyrolysis of 1 in refluxing toluene gives $(\mu\text{-H})Os_3(CO)_6(PPh_3)\{Ph_2PCH_2P(Ph)C_6H_4CNR\}$ (3) with C–C coupling between the isocyanide ligand and the activated phenyl group. The isocyanide ligand most likely plays an important role in mediating the unusual transformation of the osmium cluster. The molecular structures of $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-dppm})$ (**1b**), $(\mu\text{-H})_2Os_3(CO)_7(CNPr)\{Ph_2PCHP(Ph)C_6H_4\}$ (**2a**), and $(\mu\text{-H})Os_3(CO)_6(PPh_3)\{Ph_2PCH_2P(Ph)C_6H_4CNPr\}$ (**3a**) have been determined by X-ray diffraction studies. Crystal data are as follows. **1b**, $P2_1/n$, a = 13.432(4) Å, b = 16.963(4) Å, c = 18.183(3) Å, β = 94.91(2)°, V = 4128(2) Å^3, Z = 4, R = 6.7%, R_w = 6.7%; **2a**, $P2_1/c$, a = 11.361(5) Å, b = 13.277(3) Å, c = 28.234(7) Å, β = 96.75(3)°, V = 4229(2) Å^3, Z = 4, R = 3.2%, R_w = 2.3%; **3a**, $P2_1/n$, a = 13.110(4) Å, b = 20.149(3) Å, c = 19.126(4) Å, β = 103.49(2)°, V = 4913(2) Å^3, Z = 4, R = 3.1%, R_w = 2.6%.

Introduction

The investigation of the intramolecular activation of aliphatic and aromatic C–H bonds in transition-metal complexes has attracted considerable attention in view of its relevance to catalysis and organic synthesis.[1] Activation of aromatic C–H bonds by transition metals is more common than that of aliphatic C–H bonds, and it is rare to observe that activation of both aromatic and aliphatic C–H bonds occurs in a metal complex at the same time.[2] Continuing our evaluation of the effect of isocyanide–carbonyl replacement on the reactivity of metal isocyanide complexes $Os_3(CO)_{11}(CNR)$[3–5] and prompted as well by the derivative chemistry of $Os_3(CO)_{10}(\mu\text{-dppm})$,[6] $Ru_3(CO)_{10}(\mu\text{-dppm})$,[7] and $Ru_3(CO)_8(\mu\text{-dppm})_2$,[2a,b] we examined the influence of the coordinated isocyanide ligand on the transformation of the dppm ligand in the coordination sphere of an osmium isocyanide cluster. We observed that unusual activation of both aliphatic and aromatic C–H bonds occurs simultaneously, and C–C coupling between an activated phenyl group and the isocyanide ligand takes place as well during the transformations. The isocyanide ligand most likely plays an important role in determining the transformation and stereochemistry of the osmium cluster.

Results and Discussion

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with the dppm Ligand. Treatment of the "lightly stabilized" clusters

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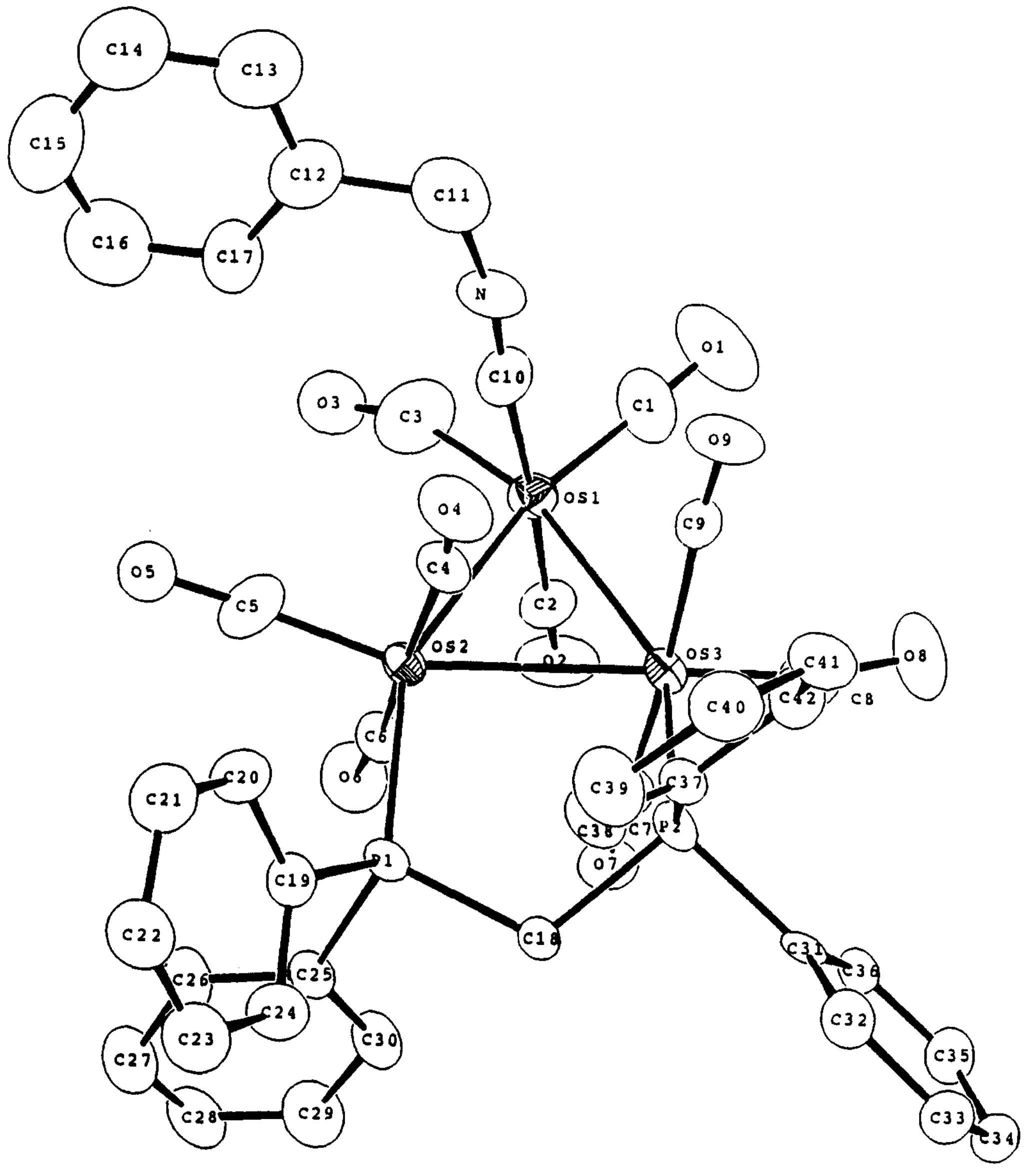
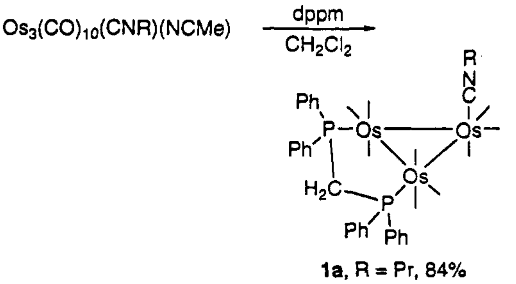


Figure 1. Molecular structure of $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-dppm})$ (**1b**) and the atomic numbering scheme.

$Os_3(CO)_{10}(CNR)(NCMe)$[5] with the dppm ligand (dppm = bis(diphenylphosphino)methane)[8] readily yields the complexes $Os_3(CO)_9(CNR)(\mu\text{-dppm})$ (**1a**, R = Pr; **1b**, R = CH_2Ph) in good yields (eq 1). The infrared spectrum showed



(1)

1a, R = Pr, 84%
1b, R = CH_2Ph, 86%

the ν_{CN} absorption at 2191 cm^{-1}, which is characteristic of a terminally coordinated isocyanide ligand.[9] In addition to spectroscopic studies, complex **1b** was further defined by X-ray diffraction analysis. An ORTEP drawing is given in Figure 1. Pertinent crystallographic details are set out in Tables 1–3. Complex **1b** has the familiar triangular Os_3 core with the dppm ligand equatorially bridging one

Table 1. Crystal and Intensity Collection Data for $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-dppm})$ (1b), $(\mu\text{-H})_2Os_3(CO)_7(CNPr)\{Ph_2PCHP(Ph)C_6H_4\}$ (2a), and $(\mu\text{-H})Os_3(CO)_6(PPh_3)\{Ph_2PCH_2P(Ph)C_6H_4CNPr\}$ (3a)

formula	$C_{42}H_{30}NO_9P_2Os_3$	$C_{42}H_{35}NO_7P_2Os_3$	$C_{53}H_{44}NO_6P_3Os_3$
fw	1325.25	1298.28	1454.44
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	13.432(4)	11.361(5)	13.110(4)
b, Å	16.963(4)	13.277(3)	20.149(3)
c, Å	18.183(3)	28.234(7)	19.126(4)
β, deg	94.912(17)	96.75(3)	103.492(22)
V, Å^3	4127.7(17)	4229.3(23)	4913.0(20)
D_{calc}, g cm^{-3}	2.133	2.039	1.966
Z	4	4	4
μ(Mo Kα), cm^{-1}	93.5	91.2	79.0
temp	room temp	room temp	room temp
radiation	Mo Kα	Mo Kα	Mo Kα
2θ(max), deg	44.9	44.9	44.8
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
total no. of reflns	5398	5520	6415
no. of obsd rflns ($F_o > 2\sigma(F_o)$)	3643	3952	4804
no. of obsd variables	515	497	599
R	0.067	0.032	0.031
R_w	0.067	0.023	0.026
$\Delta(\rho)$, e Å^{-3}	3.480	1.070	0.750
Δ/σ_{max}	0.065	0.040	0.061
GOF	2.65	1.61	1.77

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Table 2. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-dppm})$ (1b)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.58297(8)	0.73390(7)	0.94903(6)	4.06(6)
Os(2)	0.78966(7)	0.74693(6)	1.00078(6)	2.95(5)
Os(3)	0.64875(8)	0.68155(6)	1.09529(6)	3.11(5)
P(1)	0.9164(5)	0.7577(4)	1.0953(4)	2.9(3)
P(2)	0.7806(5)	0.6464(4)	1.1806(4)	3.1(3)
C(1)	0.4535(24)	0.6992(19)	0.9398(19)	7.2(21)
C(2)	0.5450(20)	0.8306(18)	0.9963(14)	5.0(15)
C(3)	0.5857(24)	0.773(3)	0.8587(19)	10.2(27)
C(4)	0.8097(18)	0.6327(17)	0.9840(15)	4.6(15)
C(5)	0.8518(25)	0.7705(16)	0.9195(15)	5.9(17)
C(6)	0.7525(19)	0.8586(16)	1.0128(14)	4.1(14)
C(7)	0.6522(19)	0.7901(15)	1.1332(14)	4.0(13)
C(8)	0.553(3)	0.6600(17)	1.1474(17)	7.1(20)
C(9)	0.6380(19)	0.5753(16)	1.0459(14)	4.1(13)
C(10)	0.6256(20)	0.6397(19)	0.8963(15)	5.4(16)
C(11)	0.676(3)	0.5241(22)	0.8150(21)	9.0(24)
C(12)	0.7476(25)	0.5525(22)	0.7580(18)	7.4(20)
C(13)	0.776(3)	0.499(3)	0.7082(21)	9.6(25)
C(14)	0.842(3)	0.522(3)	0.6575(24)	12.7(35)
C(15)	0.877(3)	0.603(3)	0.6609(21)	11.2(31)
C(16)	0.842(3)	0.6527(23)	0.7131(20)	9.1(23)
C(17)	0.7806(21)	0.6272(19)	0.7604(17)	5.9(17)
C(18)	0.8822(17)	0.7219(14)	1.1845(13)	3.0(11)
C(19)	1.0369(19)	0.7127(15)	1.0828(14)	3.9(13)
C(20)	1.0538(20)	0.6660(17)	1.0261(14)	4.7(15)
C(21)	1.1491(22)	0.6287(18)	1.0227(16)	5.5(16)
C(22)	1.2219(22)	0.6451(20)	1.0764(17)	6.4(18)
C(23)	1.2045(22)	0.6906(21)	1.1321(17)	6.7(19)
C(24)	1.1109(20)	0.7231(16)	1.1399(15)	4.5(14)
C(25)	0.9534(18)	0.8611(15)	1.1164(14)	3.6(13)
C(26)	1.0227(21)	0.8943(16)	1.0756(16)	5.1(15)
C(27)	1.0519(23)	0.9747(19)	1.0884(18)	6.7(19)
C(28)	1.0049(22)	1.0184(16)	1.1353(18)	5.9(18)
C(29)	0.9355(24)	0.9885(18)	1.1759(19)	6.7(20)
C(30)	0.9081(19)	0.9043(16)	1.1666(15)	4.4(15)
C(31)	0.7599(16)	0.6448(13)	1.2791(12)	2.5(11)
C(32)	0.8204(20)	0.5977(15)	1.3263(14)	4.2(14)
C(33)	0.8057(19)	0.5982(18)	1.4014(14)	4.6(15)
C(34)	0.7326(21)	0.6445(17)	1.4297(14)	4.8(15)
C(35)	0.6680(21)	0.6892(16)	1.3775(14)	4.7(15)
C(36)	0.6884(18)	0.6867(14)	1.3065(12)	3.1(12)
C(37)	0.8423(17)	0.5535(14)	1.1713(13)	2.8(11)
C(38)	0.9390(19)	0.5435(15)	1.1627(16)	4.5(15)
C(39)	0.9867(22)	0.4691(17)	1.1616(18)	5.9(18)
C(40)	0.9251(22)	0.4052(17)	1.1659(16)	5.5(16)
C(41)	0.8224(21)	0.4108(17)	1.1717(15)	5.0(15)
C(42)	0.7801(20)	0.4839(16)	1.1725(15)	4.3(14)
N	0.6397(17)	0.5856(14)	0.8614(13)	5.6(13)
O(1)	0.3711(17)	0.6760(13)	0.9327(17)	10.8(19)
O(2)	0.5185(16)	0.8879(13)	1.0225(12)	8.0(13)
O(3)	0.5936(17)	0.8252(15)	0.8118(12)	8.7(14)
O(4)	0.8283(14)	0.5698(10)	0.9708(12)	6.0(12)
O(5)	0.8975(15)	0.7852(12)	0.8677(11)	6.4(12)
O(6)	0.7412(16)	0.92233(11)	1.0161(12)	6.7(12)
O(7)	0.6549(14)	0.8529(11)	1.1576(10)	5.4(10)
O(8)	0.4679(16)	0.6404(12)	1.1739(14)	8.3(15)
O(9)	0.6271(16)	0.5167(11)	1.0213(11)	6.8(12)

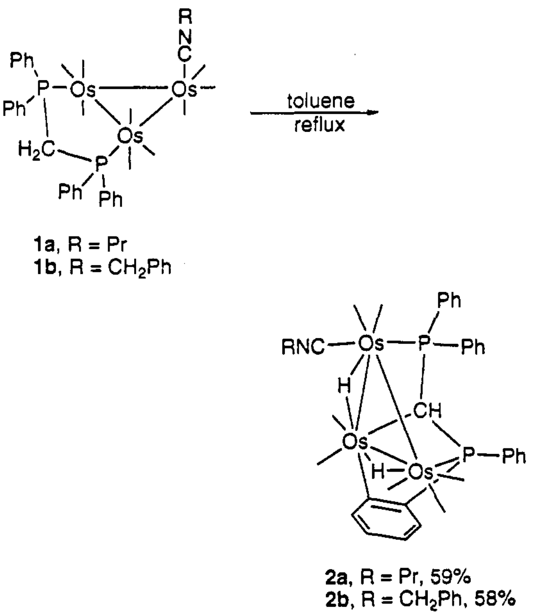
[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Os–Os vector. The isocyanide ligand occupies an axial coordination site on the third Os atom (Os(1)), as observed in several other metal isocyanide carbonyl complexes.[5,10]

Table 3. Selected Bond Distances and Angles for $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-dppm})$ (1b)

	Bond Distances (Å)		
Os(1)–Os(2)	2.8626(17)	Os(3)–P(2)	2.330(7)
Os(1)–Os(3)	2.8705(17)	P(1)–C(18)	1.828(23)
Os(1)–C(10)	1.97(3)	P(2)–C(18)	1.869(24)
Os(2)–Os(3)	2.8849(15)	C(10)–N	1.14(4)
Os(2)–P(1)	2.321(7)		
	Bond Angles (deg)		
Os(2)–Os(1)–Os(3)	60.42(4)	Os(3)–P(2)–C(18)	111.2(8)
Os(1)–Os(2)–Os(3)	59.92(4)	Os(1)–C(3)–O(3)	155(3)
Os(1)–Os(2)–P(1)	151.52(16)	Os(1)–C(10)–N	172(3)
Os(1)–Os(3)–Os(2)	59.65(4)	C(12)–C(11)–N	115(3)
Os(1)–Os(3)–P(2)	148.44(16)	P(1)–C(18)–P(2)	115.6(13)
Os(2)–P(1)–C(18)	114.0(8)	C(10)–N–C(11)	168(3)

Transformation of $Os_3(CO)_9(CNR)(\mu\text{-dppm})$ (1) in Refluxing Toluene. Thermolysis of the complexes $Os_3(CO)_9(CNR)(\mu\text{-dppm})$ in refluxing toluene produces a change in color of the solution from orange to green in 3 h. The reaction was continued for another 5 h. As the temperature is lowered, the color changes again to orange; one product was isolated in moderate yield and characterized as $(\mu\text{-H})_2Os_3(CO)_7(CNR)\{Ph_2PCHP(Ph)C_6H_4\}$ (**2a**, R = Pr; **2b**, R = CH_2Ph) (eq 2). The ^1H NMR spectrum of **2a** showed two sets of hydride peaks centered at δ −13.74 and −16.78, implying that intramolecular activation of two C–H bonds occurred in the cluster. Another set of double doublets centered at δ 5.06 which was integrated as one hydrogen atom is assigned as the *H*C group of dppm, suggesting that one of the methylene hydrogens has been activated. Each of the four well-separated multiplets centered at δ 7.60, 6.92, 6.65, and 6.01, corresponding to one of the four protons of the metalated C_6H_4 group, was assigned unambiguously by 2D NMR experiments (HMBC and HMQC methods).[11] The ^{31}P NMR spectrum of **2a** showed two doublet resonances at δ −14.58 and −62.70 corresponding to two P atoms. The extraordinary high-field ^{31}P NMR shift (δ −62.70) is of interest. To our knowledge, this is the first example of a P atom of a coordinated dppm ligand possessing such a high-field shift, suggesting that an unusual ring-size effect[12] of the dppm ligand exists in the molecule.



1a, R = Pr
1b, R = CH2Ph

2a, R = Pr, 59%
2b, R = CH2Ph, 58%

(2)

An X-ray crystal analysis of complex **2a** was undertaken. An ORTEP drawing is shown in Figure 2, and relevant crystallographic details are given in Tables 4 and 5. The molecule consists of a triangular cluster of osmium atoms with distances Os(1)–Os(2) = 2.978(1) Å, Os(2)–Os(3) = 3.037(1) Å, and Os(1)–Os(3) = 2.9585(9) Å. The isocyanide ligand occupies an axial position on Os(1). The two hydride

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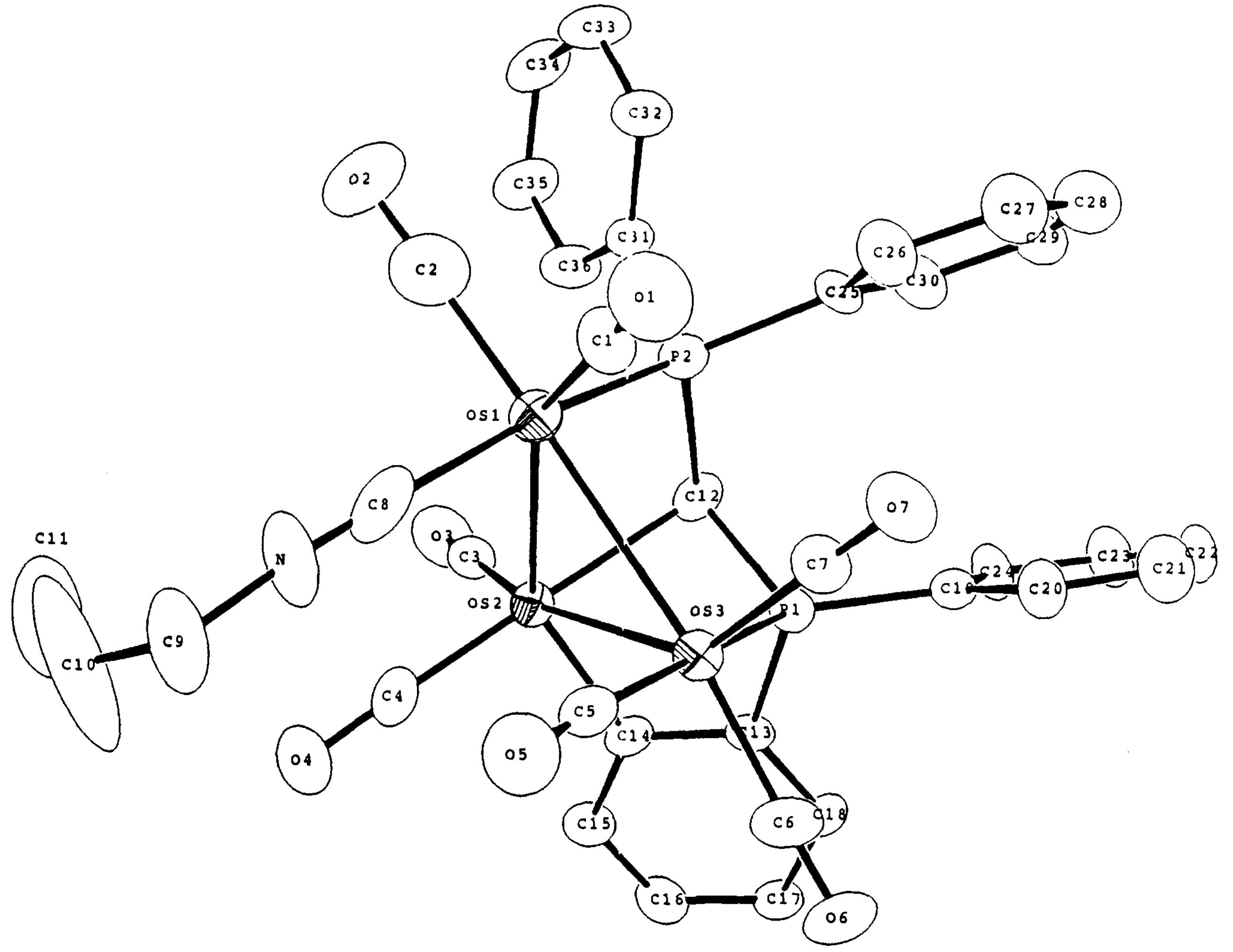
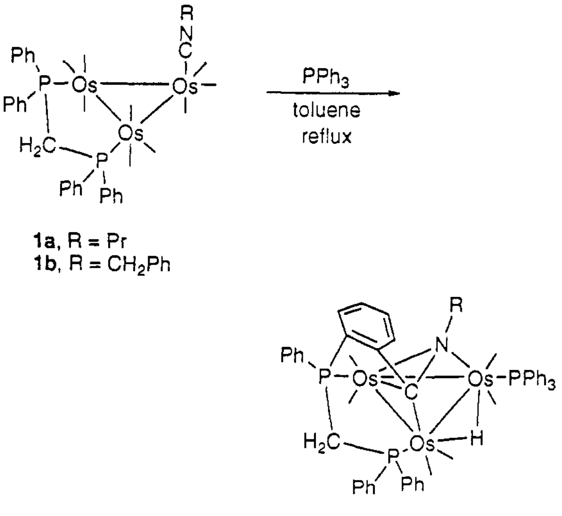


Figure 2. Molecular structure of (μ-H)$_2$Os$_3$(CO)$_7$(CNPr){Ph$_2$PCHP(Ph)C$_6$H$_4$} (**2a**) and the atomic numbering scheme.

ligands were not located in the structure determinations, but the relatively long Os(1)–Os(2) and Os(2)–Os(3) separations suggest that the hydrogen atoms bridge these bonds.[10,13] The dppm ligand has transformed to form a unique μ_3-η^4 coordination mode with two phosphorus atoms coordinating axially at the Os(1)–Os(3) vector. The C(12) of the methylene group of the dppm ligand occupies an axial coordination site on Os(2). The structure shows that two kinds of C–H activation, ortho metalation of one of the phenyl groups as well as the unusual activation of the methylene bridge of dppm, occur in the transformation, in accordance with the ^{1}H NMR analysis. It is of interest to note that both the linear isocyanide ligand and a phosphorus atom of the activated dppm group occupy the two axial coordination sites on Os(1). Compared to the starting compound **1**, the linear isocyanide ligand most likely undergoes an intramolecular rearrangement from one Os metal center to the other. Three fused rings, four-, five-, and six-membered, are connected sequentially by edge sharing. The severe twist of the rings suggests the unusual ring-size effect of the μ_3-η^4-coordinated dppm ligand and reflects the unusual upfield ^{31}P absorption of the phosphorus atom in the ^{31}P NMR spectrum.

Reaction of Os$_3$(CO)$_9$(CNR)(μ-dppm) (1) with PPh$_3$ in Refluxing Toluene. Thermolysis of **1** in refluxing toluene in the presence of PPh$_3$ gives the unprecedented complexes (μ-H)Os$_3$(CO)$_6$(PPh$_3$){Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$-CNR} (**3a**, R = Pr; **3b**, R = CH$_2$Ph) in good yields (eq 3).



1a, R = Pr
1b, R = CH$_2$Ph

3a, R = Pr, 67%
3b, R = CH$_2$Ph, 83%

(3)

The ^{1}H NMR spectrum of **3a** showed a double doublet at δ −15.24 assigned to the bridging hydride and two multiplets at δ 5.58 and 3.52 attributed to the absorptions of the two nonequivalent hydrogen atoms of the dppm methylene group. An X-ray crystal analysis of complex **3a** was also undertaken in order to obtain unambiguous information on its molecular stereochemistry. An ORTEP drawing of **3a** is shown in Figure 3. Final atomic positional parameters are listed in Table 6; selected bond distances and angles are listed in Table 7. This molecule consists

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Table 4. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for (μ-H)$_2$Os$_3$(CO)$_7$(CNPr){Ph$_2$PCHP(Ph)C$_6$H$_4$} (2a)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.73768(5)	0.81059(4)	0.037839(18)	3.713(24)
Os(2)	0.87363(4)	0.68497(3)	0.112716(17)	3.059(21)
Os(3)	0.64717(4)	0.60737(3)	0.056776(18)	3.252(21)
P(1)	0.6440(3)	0.63967(21)	0.13978(11)	3.04(14)
P(2)	0.6721(3)	0.85297(21)	0.11164(12)	3.57(15)
C(1)	0.6033(10)	0.8378(9)	−0.0058(4)	5.1(7)
C(2)	0.8050(12)	0.9378(9)	0.0308(5)	6.8(9)
C(3)	0.9877(10)	0.7447(7)	0.1570(4)	4.2(6)
C(4)	0.9880(10)	0.6295(8)	0.0817(4)	4.1(6)
C(5)	0.6800(9)	0.5751(7)	−0.0071(5)	4.6(7)
C(6)	0.6099(11)	0.4704(8)	0.0712(4)	4.9(7)
C(7)	0.4940(10)	0.6518(8)	0.0352(4)	4.2(6)
C(8)	0.8259(10)	0.7563(9)	−0.0152(5)	5.9(7)
C(9)	0.9420(13)	0.6761(12)	−0.0796(5)	8.8(10)
C(10)	1.0576(15)	0.6779(19)	−0.0704(8)	22.6(22)
C(11)	1.1340(13)	0.7253(14)	−0.0387(6)	11.9(14)
C(12)	0.7289(9)	0.7497(7)	0.1502(4)	3.3(5)
C(13)	0.7457(9)	0.5512(7)	0.1718(4)	3.0(5)
C(14)	0.8611(9)	0.5682(7)	0.1624(3)	3.0(5)
C(15)	0.9478(9)	0.5033(7)	0.1830(4)	3.9(6)
C(16)	0.9205(10)	0.4275(8)	0.2122(4)	4.4(6)
C(17)	0.8064(10)	0.4091(7)	0.2215(4)	4.1(6)
C(18)	0.7171(10)	0.4733(7)	0.2011(4)	3.9(6)
C(19)	0.5097(9)	0.6331(7)	0.1677(4)	3.0(5)
C(20)	0.4013(10)	0.6146(8)	0.1427(4)	4.4(7)
C(21)	0.3003(10)	0.6131(9)	0.1650(5)	5.8(8)
C(22)	0.3060(10)	0.6268(9)	0.2137(5)	5.4(8)
C(23)	0.4137(10)	0.6429(9)	0.2393(4)	5.2(7)
C(24)	0.5143(10)	0.6476(8)	0.2164(4)	4.4(7)
C(25)	0.5178(9)	0.8755(7)	0.1188(4)	3.7(6)
C(26)	0.4286(11)	0.8822(9)	0.0815(4)	5.3(7)
C(27)	0.3114(11)	0.8940(9)	0.0893(5)	6.4(8)
C(28)	0.2822(12)	0.9021(10)	0.1342(5)	7.3(9)
C(29)	0.3664(12)	0.8977(9)	0.1720(5)	6.7(8)
C(30)	0.4839(10)	0.8848(9)	0.1649(4)	5.1(7)
C(31)	0.7356(10)	0.9694(7)	0.1382(4)	3.7(6)
C(32)	0.6846(10)	1.0603(8)	0.1250(5)	5.0(7)
C(33)	0.7370(12)	1.1500(8)	0.1422(5)	7.0(9)
C(34)	0.8397(12)	1.1485(8)	0.1720(4)	5.6(8)
C(35)	0.8938(12)	1.0592(8)	0.1863(5)	6.3(8)
C(36)	0.8418(11)	0.9714(8)	0.1694(5)	5.2(7)
N	0.8778(9)	0.7241(8)	−0.0451(4)	7.1(7)
O(1)	0.5220(8)	0.8497(7)	−0.0349(3)	7.8(6)
O(2)	0.8455(10)	1.0174(7)	0.0258(4)	9.7(7)
O(3)	1.0552(7)	0.7751(6)	0.1866(3)	6.2(5)
O(4)	1.0674(7)	0.5925(6)	0.0632(3)	6.8(5)
O(5)	0.6988(8)	0.5508(6)	−0.0446(3)	6.9(5)
O(6)	0.5888(8)	0.3908(5)	0.0820(3)	6.4(5)
O(7)	0.3986(7)	0.6769(6)	0.0215(3)	5.9(5)
C(37)	0.2318(12)	0.1623(9)	0.1791(6)	7.4(9)
C(38)	0.3208(14)	0.1765(11)	0.1529(5)	8.6(10)
C(39)	0.3792(14)	0.2642(11)	0.1522(6)	9.6(11)
C(40)	0.3445(14)	0.3415(10)	0.1805(6)	9.3(11)
C(41)	0.2555(12)	0.3274(9)	0.2079(5)	7.0(8)
C(42)	0.1982(12)	0.2382(10)	0.2068(5)	6.7(9)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

of a triosmium cluster with three Os–Os bonds. A bridging hydride ligand which produces a lengthening effect on the metal–metal bond (Os(1)–Os(3) = 2.9294(9) Å) was located crystallographically. The PPh$_3$ group occupies an equatorial site on Os(3). The notable feature of this structure is that a C–H activation of a phenyl group along with an unusual C–C coupling between the isocyanide ligand and the activated phenyl ring occurs during the reaction. To our knowledge, this is the first example of coupling of the aryl ring of a dppm ligand to an isocyanide ligand. The isocyanide ligand thus was transformed to produce the imidoyl group with the rearrangement of the carbon atom to vicinal Os centers.

Table 5. Selected Bond Distances and Angles for (μ-H)$_2$Os$_3$(CO)$_7$(CNPr){Ph$_2$PCHP(Ph)C$_6$H$_4$} (2a)

Bond Distances (Å)

Os(1)–Os(2)	2.9781(10)	Os(3)–P(1)	2.387(3)
Os(1)–Os(3)	2.9585(9)	P(1)–C(12)	1.756(10)
Os(1)–P(2)	2.362(3)	P(1)–C(13)	1.814(10)
Os(1)–C(8)	2.029(15)	P(2)–C(12)	1.820(10)
Os(2)–Os(3)	3.0365(13)	C(8)–N	1.167(18)
Os(2)–C(12)	2.229(11)	C(9)–N	1.434(17)
Os(2)–C(14)	2.107(10)		

Bond Angles (deg)

Os(2)–Os(1)–Os(3)	61.526(25)	Os(2)–Os(3)–P(1)	62.49(8)
Os(2)–Os(1)–P(2)	72.43(8)	P(1)–Os(3)–C(5)	169.5(3)
Os(3)–Os(1)–P(2)	84.58(7)	Os(2)–C(12)–P(1)	91.2(4)
P(2)–Os(1)–C(8)	165.9(3)	Os(2)–C(12)–P(2)	103.7(5)
Os(1)–Os(2)–Os(3)	58.92(3)	P(1)–C(12)–P(2)	112.2(5)
C(4)–Os(2)–C(12)	178.3(4)	P(1)–C(13)–C(14)	111.1(7)
Os(1)–Os(3)–Os(2)	59.555(18)	Os(2)–C(14)–C(13)	112.8(7)
Os(1)–Os(3)–P(1)	93.40(7)	C(8)–N–C(9)	174.8(13)

Proposed Transformation Mechanism of the dppm Ligand in Triosmium Clusters. Thermolysis of Os$_3$(CO)$_9$(CNR)(μ-dppm) (1) in refluxing toluene is suggested to lead initially to the loss of one CO ligand and, subsequently, to induce the ortho metalation of a dppm phenyl group. In order to characterize the intermediates of the reaction, we have concentrated the green solution of **1a** at elevated temperature (110 °C) and isolated by column chromatography a yellow-green band and a green band from the green residue. The yellow-green band contained a species with the proposed formulation (μ-H)Os$_3$(CO)$_8$(CNPr){Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$} (4). The IR spectrum of 4 showed a characteristic absorption of ν_{CN} at 2199 cm^{-1}, indicating that the isocyanide ligand is terminally coordinated at the Os center. The ^{1}H NMR spectrum showed a doublet hydride peak centered at δ −16.67 as well as the characteristic high-field resonances of the metalated C$_6$H$_4$ group at δ 6.46 and 6.10, indicating that an ortho-metalation process had taken place. This was corroborated by the observation of two sets of nonequivalent proton peaks of the dppm CH$_2$ group centered at δ 5.38 and 3.50. Thermolysis of 4 in refluxing toluene for 3 h leads to the formation of **2a** in about 80% yield as indicated by the ^{1}H NMR spectrum. This observation provides convincing evidence that complex 4 is one of the intermediates for the formation of compound **2a**. In addition to the identification of 4 from the yellow-green band, the subsequently eluted green band consisted of two major species along with slight contamination of 4. Each of these two major species bears a hydride ligand (δ −13.53 and −10.28, respectively) and an ortho-metalated C$_6$H$_4$ moiety (δ 6.50, 6.06) of the dppm group. These species are suspected to be some other intermediates of the reaction. However, due to the complexity and serious overlapping of their ^{1}H NMR spectra, we were not able to fully characterize them. Attempts to grow crystals of these species have not succeeded as yet. It is suggested that intermediate 4 continues to eliminate another CO group at elevated temperature, thus inducing the transformation of the isocyanide ligand and changing the orientation of two phosphorus atoms from equatorial to axial sites.[14] Consequently, this creates an opportunity for the dppm methylene carbon (C(12)) to access Os(2) and induce the activation of a C–H bond to form complex 2. In the presence of PPh$_3$, the reaction of 1 with dppm at elevated temperature may involve an intermediate with a triply bridging six-electron-donor CNR group,[15] which

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(14) (a) Bruce, M. I.; Humphrey, P. A.; Shawkataly, O. B.; Snow, M. R.; Tiekink, E. R. T.; Cullen, W. R. *Organometallics* **1990**, *9*, 2910. (b) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Organometallics* **1992**, *11*, 853.

(15) (a) Bruce, M. I.; Hambley, T. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 353. (b) Bruce, M. I.; Hambley, T. W.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1983**, 2385.

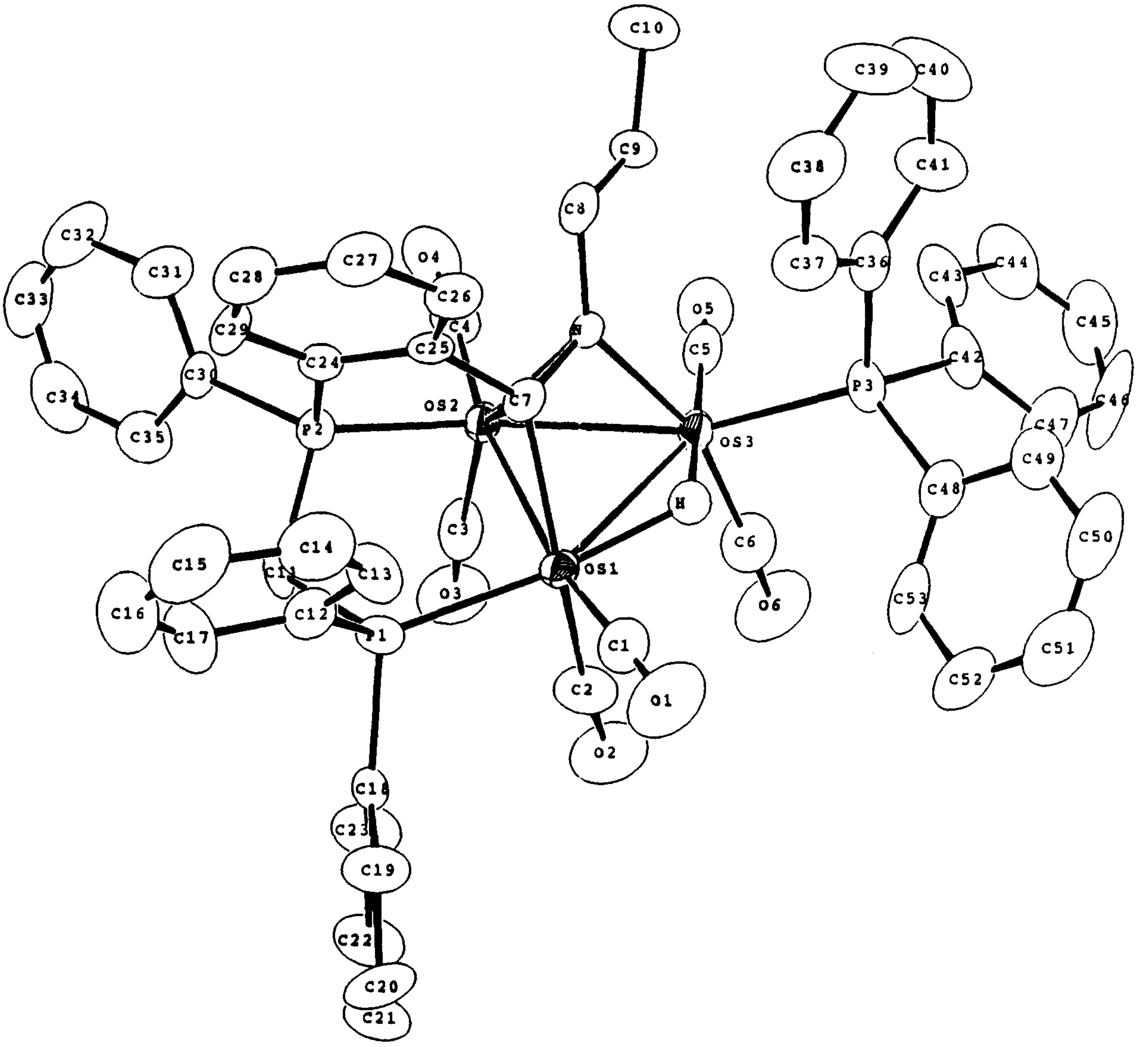

Figure 3. Molecular structure of (μ-H)$Os_3(CO)_6(PPh_3)\{Ph_2PCH_2P(Ph)C_6H_4CNPr\}$ (**3a**) and the atomic numbering scheme.

provides a feasible pathway for the rearrangement of the isocyanide ligand to the vicinal Os atoms. The formation of the imidoyl group via a C–C coupling may be attributed to the combination of an ortho-metalated phenyl ring and an isocyanide ligand by an insertion reaction to yield complex 3.

It is worthwhile to compare the reactivity of $Os_3(CO)_9(CNR)(\mu\text{-dppm})$ (1) with the derivative chemistry of the clusters $Os_3(CO)_{10}(\mu\text{-dppm})$, $Ru_3(CO)_{10}(\mu\text{-dppm})$, and $Ru_3(CO)_8(\mu\text{-dppm})_2$. On thermolysis, the complexes $Os_3(CO)_{10}(\mu\text{-dppm})$[6] and $Ru_3(CO)_{10}(\mu\text{-dppm})$[7] undergo ortho metalation of one of the dppm phenyl groups to afford $(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}$[7] and $Ru_3(CO)_9\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}$,[6] respectively. Pyrolysis of $Ru_3(CO)_8(\mu\text{-dppm})_2$[2a,b] at 95 °C gives $(\mu\text{-H})Ru_3(CO)_7\{\mu_3\text{-}\eta^4\text{-Ph}_2PCHP(Ph)C_6H_4\}(\mu\text{-dppm})$, involving C–H activations of both the phenyl and methylene groups of the dppm ligand. In our observations, the complex $Os_3(CO)_9(CNR)(\mu\text{-dppm})$ (1) on pyrolysis also undergoes activation of a phenyl group as well as one methylene C–H bond of the dppm group and even a novel C–C coupling between the isocyanide and the activated phenyl group in the presence of PPh_3. Although isocyanide and CO are isoelectronic and similar in composition and structure,[16] the isocyanide ligand in complex 1 most likely plays a key role in mediating the reactivity and the stereochemistry of the osmium cluster.

Experimental Section

General Data. The complexes $Os_3(CO)_{11}(CNPr)$ and $Os_3(CO)_{11}(CNCH_2Ph)$ were prepared previously.[3] Other reagents were purchased from commercial sources and were used as received. All manipulations were performed with standard Schlenk techniques. Solvents were dried by stirring over Na/benzophenone (ether) or CaH_2 (hexane, CH_2Cl_2, CH_3CN, toluene) and were freshly distilled prior to use. IR spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Bruker AC-200, ACP-300, or AMX-500 FT NMR spectrometer, and mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The ^{31}P chemical shifts are referenced with respect to external 85% H_3PO_4.

Reaction of $Os_3(CO)_{10}(CNR)(NCMe)$ with the dppm Ligand. A solution of $Os_3(CO)_{11}(CNPr)$ (54 mg, 0.06 mmol) in CH_2Cl_2 (40 mL) and acetonitrile (1 mL) was treated with a solution of Me_3NO (6 mg, 0.08 mmol) in 20:100 CH_3CN/CH_2Cl_2 (3 mL). The mixture was stirred for 30 min at room temperature and filtered through a small silica column. The solvent was removed under vacuum, and the residue was redissolved in 40 mL of CH_2Cl_2. The resulting solution of $Os_3(CO)_{10}(CNPr)(NCMe)$ was treated with dppm (25 mg, 0.06 mmol) and stirred for 8 h. The solvent was removed under vacuum, and the residue was

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(16) Kuty, D. W.; Alexander, J. J. *Inorg. Chem.* **1978**, *17*, 1489.

Table 6. Atomic Coordinates and Isotropic Thermal Parameters (Å²) for (μ-H)$Os_3(CO)_6(PPh_3)\{Ph_2PCH_2P(Ph)C_6H_4CNPr\}$ (3a)

atom	*x*	*y*	*z*	B_{iso}[a]
Os(1)	0.58465(3)	0.372346(22)	0.201899(22)	1.986(19)
Os(2)	0.64945(4)	0.429321(22)	0.338855(22)	2.034(19)
Os(3)	0.45357(3)	0.375474(23)	0.306688(23)	2.283(20)
P(1)	0.74528(23)	0.39372(14)	0.17309(14)	2.39(13)
P(2)	0.77713(23)	0.48535(14)	0.29917(15)	2.36(14)
P(3)	0.27332(23)	0.37533(18)	0.25455(16)	3.00(16)
C(1)	0.5212(9)	0.3505(5)	0.1068(5)	2.9(6)
C(2)	0.6228(10)	0.2821(5)	0.2251(6)	3.9(7)
C(3)	0.7320(8)	0.3560(6)	0.3741(5)	3.5(6)
C(4)	0.6693(9)	0.4703(6)	0.4281(5)	3.3(6)
C(5)	0.4477(9)	0.3884(5)	0.4010(5)	3.2(6)
C(6)	0.4592(10)	0.2830(6)	0.3258(6)	4.5(7)
C(7)	0.5599(8)	0.4679(5)	0.2344(5)	2.1(5)
C(8)	0.4651(9)	0.5409(5)	0.3028(5)	2.9(5)
C(9)	0.4169(9)	0.5409(5)	0.3680(6)	3.3(6)
C(10)	0.3618(11)	0.6066(6)	0.3739(7)	5.4(8)
C(11)	0.8442(7)	0.4286(5)	0.2496(5)	2.5(5)
C(12)	0.7534(9)	0.4528(5)	0.1008(5)	3.2(6)
C(13)	0.6627(9)	0.4764(6)	0.0543(5)	3.4(6)
C(14)	0.6687(10)	0.5233(6)	0.0040(6)	4.3(7)
C(15)	0.7654(11)	0.5467(6)	−0.0011(6)	5.4(8)
C(16)	0.8566(10)	0.5211(7)	0.0420(6)	5.2(8)
C(17)	0.8509(9)	0.4740(6)	0.0920(6)	4.6(8)
C(18)	0.8033(8)	0.3181(5)	0.1456(5)	2.7(5)
C(19)	0.7914(10)	0.3025(6)	0.0736(6)	4.1(6)
C(20)	0.8259(11)	0.2433(6)	0.0533(6)	4.8(7)
C(21)	0.8728(10)	0.1988(6)	0.1027(6)	4.8(7)
C(22)	0.8878(10)	0.2131(6)	0.1738(7)	5.3(8)
C(23)	0.8536(10)	0.2714(6)	0.1952(6)	4.5(7)
C(24)	0.7105(8)	0.5441(5)	0.2309(5)	2.2(5)
C(25)	0.6038(8)	0.5312(5)	0.2069(5)	2.4(5)
C(26)	0.5419(8)	0.5705(5)	0.1534(5)	2.7(5)
C(27)	0.5881(9)	0.6220(6)	0.1251(5)	3.6(6)
C(28)	0.6935(9)	0.6353(6)	0.1476(5)	3.6(6)
C(29)	0.7542(9)	0.5958(5)	0.2000(5)	3.1(6)
C(30)	0.8845(8)	0.5314(5)	0.3570(5)	2.3(5)
C(31)	0.8764(10)	0.5979(6)	0.3709(6)	4.4(7)
C(32)	0.9587(11)	0.6325(7)	0.4137(6)	5.7(8)
C(33)	1.0471(10)	0.6002(7)	0.4433(6)	6.0(8)
C(34)	1.0585(10)	0.5354(7)	0.4316(6)	5.9(8)
C(35)	0.9770(9)	0.5001(6)	0.3884(6)	4.5(7)
C(36)	0.2174(8)	0.4574(5)	0.2271(5)	3.2(6)
C(37)	0.2572(10)	0.4919(6)	0.1757(6)	4.4(7)
C(38)	0.2154(11)	0.5526(6)	0.1504(6)	5.6(8)
C(39)	0.1382(12)	0.5804(7)	0.1773(7)	6.9(9)
C(40)	0.0998(11)	0.5493(7)	0.2275(8)	7.3(10)
C(41)	0.1372(11)	0.4875(6)	0.2532(6)	5.1(7)
C(41)	0.1940(8)	0.3421(6)	0.3137(5)	3.3(6)
C(43)	0.1952(9)	0.3729(7)	0.3789(6)	4.7(7)
C(44)	0.1392(10)	0.3450(7)	0.4252(6)	5.7(8)
C(45)	0.0836(11)	0.2890(7)	0.4072(7)	6.6(9)
C(46)	0.0841(11)	0.2584(8)	0.3472(7)	7.6(10)
C(47)	0.1379(11)	0.2820(7)	0.2981(6)	5.4(8)
C(48)	0.2252(9)	0.3285(5)	0.1714(5)	3.0(6)
C(49)	0.1250(9)	0.3397(6)	0.1273(6)	4.3(7)
C(50)	0.0911(10)	0.3093(7)	0.0616(6)	5.7(8)
C(51)	0.1523(12)	0.2672(7)	0.0372(7)	6.1(8)
C(52)	0.2493(11)	0.2545(7)	0.0777(7)	5.7(8)
C(53)	0.2853(10)	0.2849(6)	0.1443(6)	4.8(7)
N	0.5001(6)	0.4737(4)	0.2853(4)	2.2(4)
O(1)	0.4826(7)	0.3347(4)	0.0483(4)	5.6(5)
O(2)	0.6380(8)	0.2280(4)	0.2435(5)	6.4(6)
O(3)	0.7789(7)	0.3087(4)	0.3961(4)	5.8(5)
O(4)	0.6858(7)	0.4987(5)	0.4828(4)	5.7(5)
O(5)	0.4484(7)	0.3910(4)	0.4625(4)	5.1(5)
O(6)	0.4692(8)	0.2291(4)	0.3406(5)	7.6(7)
H	0.458(6)	0.366(4)	0.226(4)	2.4

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 7. Selected Bond Distances and Angles for (μ-H)$Os_3(CO)_6(PPh_3)\{Ph_2PCH_2P(Ph)C_6H_4CNPr\}$ (3a)

	Bond Distances (Å)		
Os(1)–Os(2)	2.8041(8)	C(7)–C(25)	1.541(14)
Os(1)–Os(3)	2.9294(9)	C(7)–N	1.391(11)
Os(1)–P(1)	2.338(3)	C(8)–N	1.493(13)
Os(1)–C(7)	2.072(10)	C(24)–C(25)	1.391(15)
Os(2)–Os(3)	2.7227(10)	C(24)–C(29)	1.385(14)
Os(2)–P(2)	2.290(3)	C(25)–C(26)	1.394(14)
Os(2)–C(7)	2.210(9)	C(26)–C(27)	1.374(15)
Os(2)–N	2.178(8)	C(27)–C(28)	1.374(17)
Os(3)–P(3)	2.341(3)	C(28)–C(29)	1.378(16)
Os(3)–N	2.137(8)		
	Bond Angles (deg)		
Os(2)–Os(1)–Os(3)	56.652(21)	Os(1)–C(7)–Os(2)	81.7(3)
Os(2)–Os(1)–P(1)	92.96(7)	Os(1)–C(7)–C(25)	124.7(6)
Os(2)–Os(1)–C(7)	51.3(3)	Os(1)–C(7)–N	116.1(6)
Os(3)–Os(1)–P(1)	149.52(7)	Os(2)–C(7)–C(25)	115.9(7)
Os(3)–Os(1)–C(7)	67.48(25)	Os(2)–C(7)–N	70.3(5)
P(1)–Os(1)–C(7)	96.4(3)	C(25)–C(7)–N	119.1(8)
Os(1)–Os(2)–Os(3)	63.995(24)	P(1)–C(11)–P(2)	108.3(5)
Os(1)–Os(2)–P(2)	88.73(7)	Os(2)–N–C(7)	72.8(5)
Os(1)–Os(2)–N	71.68(19)	Os(2)–N–C(8)	123.8(6)
Os(3)–Os(2)–N	50.22(20)	Os(3)–N–C(7)	106.8(6)
C(7)–Os(2)–N	36.9(3)	Os(3)–N–C(8)	132.9(6)
Os(1)–Os(3)–Os(2)	59.352(23)	C(7)–N–C(8)	119.0(7)
Os(2)–P(2)–C(11)	109.8(3)		

chromatographed on a silica gel TLC plate with 10:90 ether/hexane as eluent to give $Os_3(CO)_9(CNPr)(\mu\text{-dppm})$ (**1a**; 60 mg, 0.05 mmol, 84%). Anal. Calcd for $C_{38}H_{29}NO_9P_2Os_3$: C, 35.75; H, 2.27. Found: C, 36.59; H, 2.35. IR (CH_2Cl_2): ν_{CN} 2191 (w), ν_{CO} 2064 (vw), 2053 (m), 2010 (s), 1995 (vs), 1980 (s), 1945 (m), 1927 (sh) cm⁻¹. ¹H NMR ($CDCl_3$): δ 7.44–7.30 (m, Ph), 5.05 (t, 2 H, CH_2P, J_{HP} = 10.5 Hz), 3.98 (t, 2 H, NCH_2), 1.74 (m, 2 H, CH_2CH_3), 1.02 (t, 3 H, CH_3). ³¹P NMR ($CDCl_3$): δ −28.14 (s, 2 P).

The complex $Os_3(CO)_9(CNCH_2Ph)(\mu_2\text{-dppm})$ (**1b**) was obtained under reaction conditions similar to those for **1a** in 86% yield based on $Os_3(CO)_{11}(CNCH_2Ph)$. Anal. Calcd for $C_{42}H_{29}NO_9P_2Os_3$: C, 38.08; H, 2.19. Found: C, 38.09; H, 1.81. **1b**: IR (CH_2Cl_2) ν_{CN} 2190 (w), ν_{CO} 2068 (vw), 2055 (m), 2012 (s), 2000 (vs), 1983 (s), 1952 (m), 1934 (sh) cm⁻¹; ¹H NMR ($CDCl_3$) δ 7.35–7.19 (m, Ph), 3.98 (t, 2 H, NCH_2), 4.99 (t, 2 H, CH_2P, J_{HP} = 10.5 Hz); ³¹P NMR ($CDCl_3$) δ −27.99 (s, 2 P).

Preparation of (μ-H)$_2$Os$_3$(CO)$_7$(CNCH$_2$Ph){Ph$_2$PCH(Ph)C$_6$H$_4$} (2b). Thermolysis of the complex $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-dppm})$ (**1b**; 80 mg, 0.06 mmol) in refluxing toluene (150 mL) resulted in a color change from orange to green in 3 h. The reaction was continued for another 5 h; the color changes to orange on cooling. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 20% diethyl ether/hexane as eluent to give **2b** (44 mg, 0.04 mmol, 58%). Anal. Calcd for $C_{40}H_{29}NO_7P_2Os_3$: C, 37.87; H, 2.29. Found: C, 38.04; H, 2.73. IR (CH_2Cl_2): ν_{CN} 2194 (w), ν_{CO} 2079 (w), 2057 (m), 2008 (vs), 1983 (s), 1957 (m), 1939 (w) cm⁻¹. ¹H NMR ($CDCl_3$) δ 7.62–6.68 (m, Ph and C_6H_4), 6.01 (m, 1 H, C_6H_4), 5.07 (dd, 1 H, CH, J_{HP} = 11.8 Hz, $J_{HP'}$ = 4.2 Hz), 5.01 (s, 2 H, $CNCH_2$), −13.74 (d, 1 H, Os–H–Os, J_{HP} = 12.8 Hz), −16.78 (dd, 1 H, Os–H–Os, J_{HP} = 11.5 Hz, $J_{HP'}$ = 5.0 Hz). ³¹P NMR ($CDCl_3$): δ −14.80 (d, 1 P, J_{PP} = 56.0 Hz), −62.61 (d, 1 P).

The complex $(\mu\text{-H})_2Os_3(CO)_7(CNPr)\{Ph_2PCH(PH)C_6H_4\}$ (**2a**) was obtained under reaction conditions similar to those for **2b** in 59% yield based on $Os_3(CO)_9(CNPr)(\mu_2\text{-dppm})$. **2a**: IR ($CH_2Cl_2$) ν_{CN} 2198 (w), ν_{CO} 2078 (vw), 2057 (m), 2009 (vs), 1985 (s), 1949 (m), 1940 (w) cm⁻¹; ¹H NMR ($CDCl_3$) δ 7.62–6.63 (m, Ph and C_6H_4), 6.01 (m, 1 H, C_6H_4), 5.06 (dd, 1 H, CH, J_{HP} = 11.7 Hz, $J_{HP'}$ = 4.2 Hz), 3.75 (t, 2 H, $CNCH_2$), 1.66 (m, 2 H, CH_2CH_3), 0.94 (t, 3 H, CH_3), −13.74 (d, 1 H, Os–H–Os, J_{HP} = 12.8 Hz), −16.78 (dd, 1 H, Os–H–Os, J_{HP} = 11.5 Hz, $J_{HP'}$ = 5.0 Hz); ³¹P NMR ($CDCl_3$) δ −14.58 (d, 1 P, $J_{PP'}$ = 56.2 Hz), −62.70 (d, 1 P).

Reaction of $Os_3(CO)_9(CNPr)(\mu\text{-dppm})$ (1a) with PPh$_3$ in Refluxing Toluene. Thermolysis of the complex $Os_3(CO)_9(CNPr)(\mu\text{-dppm})$ (**1a**; 40 mg, 0.03 mmol) with PPh_3 (8 mg, 0.03 mmol) in refluxing toluene (50 mL) for 3 h was accompanied by a color change to deep orange. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 30% CH_2Cl_2/hexane as eluent to give (μ-H)$Os_3(CO)_6(PPh_3)\{Ph_2PCH_2P(Ph)C_6H_4CNPr\}$ (**3a**; 30 mg, 0.02 mmol, 67%). Anal. Calcd for $C_{53}H_{44}NO_6P_3Os_3$: C, 43.77; H, 3.05. Found: C, 43.25; H, 2.49. IR (CH_2Cl_2): ν_{CO} 2007 (vs), 1999 (sh), 1980 (s), 1943 (sh), 1933 (s), 1913 (m), 1899 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.65–7.07 (m, Ph and C$_6$H$_4$), 6.41, 6.16 (m, 1 H, 1 H, C$_6$H$_4$), 5.58 (m, 1 H, C*H*HP), 3.52 (m, 1 H, CH*H*P, $J_{HH'}$ = 12.8 Hz, J_{HP} = 10.1 Hz), 2.11 (m, 2 H, CNCH$_2$), 1.03 (m, 2 H, C*H*$_2$CH$_3$), 0.33 (t, 3 H, CH$_3$), −15.24 (dd, 1 H, Os–H–Os, J_{HP} = 39.2 Hz, $J_{HP'}$ = 15.9 Hz). ^{31}P NMR (CDCl$_3$): δ 5.14 (d, 1 P, J_{PP} = 44.5 Hz), −0.50 (s, 1 P), −18.27 (d, 1 P).

Reaction of Os$_3$(CO)$_9$(CNCH$_2$Ph)(μ-dppm) (1b) with PPh$_3$ in Refluxing Toluene. Thermolysis of **1b** (45 mg, 0.04 mmol) with PPh$_3$ (10 mg, 0.04 mmol) in refluxing toluene (50 mL) for 3 h resulted in a color change to deep orange. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate with 40% CH$_2$Cl$_2$/hexane as eluent to give (μ-H)Os$_3$(CO)$_6$(PPh$_3$){Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$CNCH$_2$Ph} (**3b**; 44 mg, 0.03 mmol, 84%). IR (CH$_2$Cl$_2$): ν_{CO} 2008 (vs), 1985 (s), 1946 (sh), 1934 (s), 1914 (m), 1902 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.59–6.98 (m, Ph and C$_6$H$_4$), 6.45, 6.17 (m, 1 H, 1 H, C$_6$H$_4$), 5.48 (m, 1 H, C*H*HP), 3.54 (s, 2 H, CH$_2$Ph), 3.42 (m, 1 H, CH*H*P), −15.40 (dd, 1 H, Os–H–Os, J_{HP} = 39.3 Hz, $J_{HP'}$ = 17.1 Hz). ^{31}P NMR (CDCl$_3$): δ 5.52 (d, 1 P, J_{PP} − 43.7 Hz), −0.27 (s, 1 P), −18.64 (d, 1 P).

Isolation of Intermediates. Thermolysis of Os$_3$(CO)$_9$(CNPr)(μ-dppm) (**1a**; 200 mg, 0.16 mmol) in refluxing toluene (5 mL) for 4 h was followed by the removal of solvent slowly under vacuum at elevated temperature (110 °C). The solution remained green during the process of concentration. The green residue was chromatographed on a silica gel TLC plate with 20% CH$_2$Cl$_2$/hexane as eluent to give, in order of elution, 6 mg of yellow (μ-H)$_2$Os$_3$(CO)$_7$(CNPr){Ph$_2$PCHP(Ph)C$_6$H$_4$} (**2a**), 14 mg of a yellow-green compound with the proposed formulation (μ-H)Os$_3$(CO)$_8$(CNPr){Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$} (**4**) (contaminated with about 10% of the next eluted compound), 16 mg of a green species, 90 mg of orange Os$_3$(CO)$_9$(CNPr)(μ-dppm) (**1a**), and a trace amount of an unidentified green species. The band of complex **4** and the following green band are eluted very closely and obtained slightly cross-contaminated. The latter green band was a mixture containing about 45% of a major species, 40% of another compound, and 15% of **4** as indicated by the ^{1}H NMR spectrum. The ^{1}H NMR spectrum (in CDCl$_3$) of this green band showed three sets of hydride peaks at δ −16.67 (d), −13.53 (dd), and −10.28 (dd) for complex **4**, the major species, and the other compound, respectively. We were not able to assign other peaks unambiguously due to the serious overlapping and complexity of the spectrum, but the characteristic absorption pattern of phenyl peaks (δ 6.50, 6.06) indicates that one of the phenyl groups of dppm has been activated to give the C$_6$H$_4$ moiety. Spectroscopic data for **4**: IR (CH$_2$Cl$_2$) ν_{CN} 2199 (w), ν_{CO} 2053 (w), 2015 (vs), 2000 (s), 1974 (m), 1953 (m); ^{1}H NMR (CDCl$_3$) δ 8.06–6.81, 6.46, 6.10 (m, Ph and C$_6$H$_4$), 5.38 (m, 1 H, C*H*HP), 3.86 (m, 2 H, CNCH$_2$), 3.50 (m, 1 H, CH*H*P, $J_{HH'}$ = 12.7 Hz, J_{HP} = 9.6 Hz), 1.69 (m, 2 H, C*H*$_2$CH$_3$), 0.87 (t, 3 H, CH$_3$), −16.67 (d, 1 H, Os–H–Os, J_{HP} = 8.1 Hz).

Thermolysis of the Intermediate 4 in Refluxing Toluene. A solution of complex **4** (8 mg, contaminated with about 10% of the next eluted green species) in toluene (3 mL) was refluxed at 110 °C for 3 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum. The ^{1}H NMR spectrum of the residue showed that the complex (μ-H)$_2$Os$_3$(CO)$_7$(CNPr){Ph$_2$PCHP(Ph)C$_6$H$_4$} (**2a**) was obtained in about 80% yield.

Crystallographic Structure Determination. Crystals of both Os$_3$(CO)$_9$(CNCH$_2$Ph)(μ-dppm) (**1b**) and (μ-H)Os$_3$(CO)$_6$(PPh$_3$){Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$CNPr} (**3a**) were grown from CH$_2$Cl$_2$/hexane solutions at −5 °C. Crystals of (μ-H)$_2$Os$_3$(CO)$_7$(CNPr){Ph$_2$PCHP(Ph)C$_6$H$_4$} (**2a**) were grown from CH$_2$Cl$_2$/benzene/hexane solution. Specimens of suitable quality were mounted in thin-walled glass capillaries and used for measurement of precise cell constants and intensity data collection. All diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.70930 Å) with a θ–2θ scan mode. Unit cells were determined and refined using 25 randomly selected reflections obtained with the CAD-4 automatic search, center, index, and least-squares routines. Anomalous dispersion corrections were applied to all non-hydrogen atoms. Lorentz/polarization (*Lp*) and empirical absorption corrections based on three azimuthal scans were applied to the data for each structure. Compounds **1b**, **2a**, and **3a** crystallized in the monoclinic crystal system. The systematic absences in the diffraction data of **1b**, **2a**, and **3a** unambiguously established the space group as $P2_1/n$, $P2_1/c$ and $P2_1/n$, respectively. The structures were solved in the heavy-atom method. All remaining non-hydrogen atoms were located from the difference Fourier map, and they were included in the final refinement cycle and refined by full-matrix least squares. A benzene solvent packs in the lattice along with a molecule of **2a**, but there are no interactions between them. The hydride peak in **3a** was located and refined. All of the data processing was carried out on a Microvax 3600 using the NRCC SDP program.[17]

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Supplementary Material Available: Tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles for **1b**, **2a**, and **3a** (22 pages). Ordering information is given on any current masthead page.

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[17] Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3; Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Clarendon Press; Oxford, England, 1985; pp 167–174.