Synthesis of the $N(CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2)_3$ Ligand and Its Complexation with Tungsten Carbonyls To Form a 47-Membered Cryptand-Like Metallatricycle

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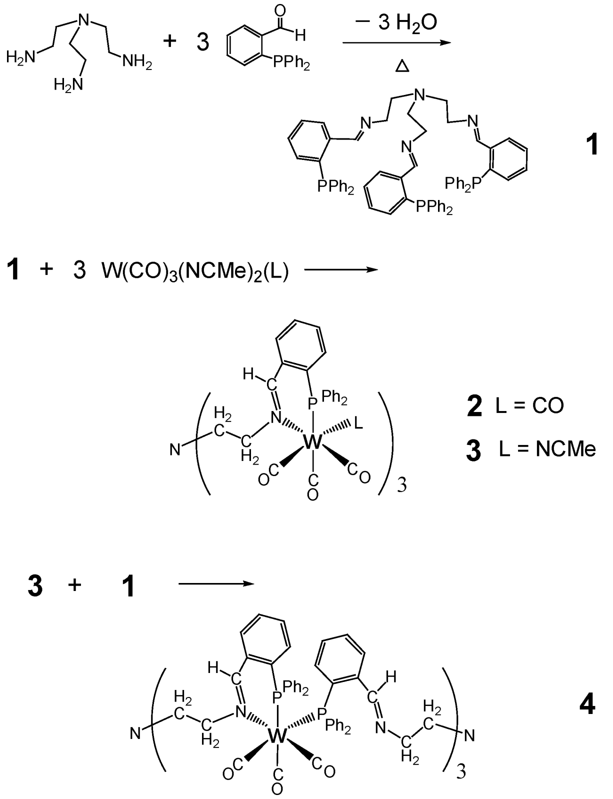
Received April 13, 2005

Summary: Schiff base condensation of $N(CH_2CH_2NH_2)_3$ *and* $Ph_2P(o\text{-}C_6H_4)C({=}O)H$ *produces the potentially heptadentate ligand* $N(CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2)_3$*, which reacts with tungsten carbonyls to form two tripodal complexes and a tricyclic cage complex.*

Recent work on assembly of metal complexes (or ions) with suitable polydentate ligands allows the preparation of well-defined inorganic 2-D and 3-D supramolecular architectures in solution.[1,2] Several factors, such as the design of ligands, the mode of coordination by the metal atom, the metal-to-ligand ratio, and the presence of guest molecules, are crucial to the structure and properties of the final assemblies.[3−10] Thus far, most of the effort has been directed to the use of mononuclear metal ions (especially Pd^{2+} and Pt^{2+})[3,4] or dinuclear ion centers (Rh_2^{4+}, Mo_2^{4+}),[6,11] while the zero-valence organometallic species, in particular the metal carbonyls, are seldom selected as the geometry-setting metal components.[12−15] Herein we present the synthesis of a new tripodal ligand[16] and its coordination to tungsten carbonyls, leading to a cryptand-like cage complex. The results are summarized in Scheme 1.

Schiff base[17] condensation of $N(CH_2CH_2NH_2)_3$ and 3 equiv of $Ph_2P(o\text{-}C_6H_4)C({=}O)H$ in refluxing benzene gave the expected tripodal compound $N(CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2)_3$ (**1**; 82%)[18] as an air-stable, pale yellow crystalline solid after crystallization from *n*-hexane. A few pellets of 3 Å molecular sieves must be added to remove the water generated from the condensation reaction; otherwise, low yields of **1** resulted. Compound **1** contains three iminophosphino groups connected to a nonrigid triethyleneamine spacer. The IR spectrum in KBr depicts the N=C stretching at 1641 cm^{-1}. The ^1H NMR spectrum shows a doublet signal at δ 8.80 for the imine protons with $^4J_{P-H} = 5$ Hz, a multiplet in the

Scheme 1



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[18] Anal. Calcd for $C_{63}H_{57}N_4P_3$: C, 78.57; H, 5.97; N, 5.82. Found: C, 79.20; H, 6.21; N, 5.85. MS (FAB): *m/z* 963 (M^+). IR (KBr): 1641 (N=C) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 8.80 (d, 3H, $^4J_{P-H} = 5$ Hz, N=CH), 7.92 (m, 3H, Ph), 7.37−7.23 (m, 36 H, Ph), 6.85 (m, 3H, Ph), 3.39 (t, 6H, $^3J_{H-H} = 7$ Hz, CH_2), 2.45 (t, 6H, $^3J_{H-H} = 7$ Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ −13.02 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 160.3 (d, $^3J_{P-C} = 21$ Hz, N=CH), 139.5−127.5 (m, Ph), 59.4 (s, CH_2), 54.7 (s, CH_2).

10.1021/om050281p CCC: $30.25

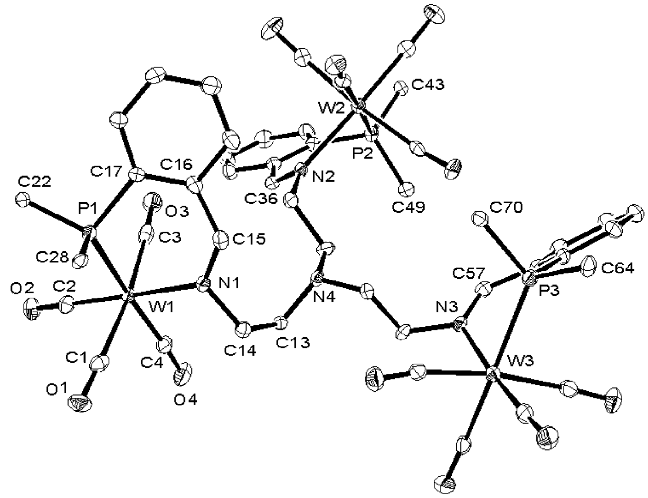

Figure 1. Molecular structure of **2**. The C_6H_5 groups have been artificially omitted, except for the ipso carbon atoms, for clarity.

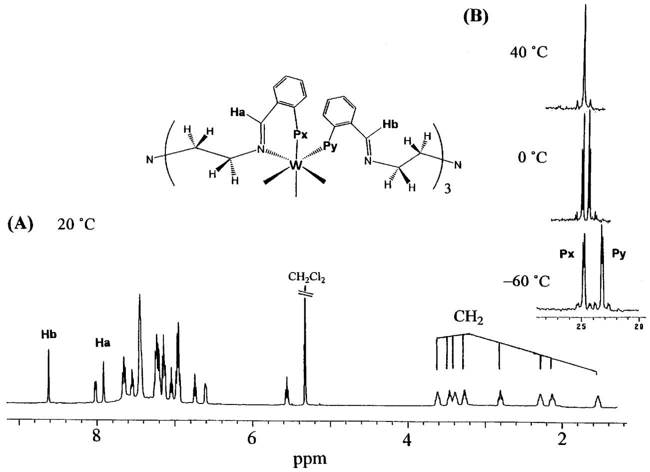

Figure 2. ^1H (A) and variable-temperature $^{31}P\{^1H\}$ (B) NMR spectra of **4** in CD_2Cl_2.

range δ 7.92−6.85 for the phenyl protons, and two triplet signals at δ 3.39 and 2.45, with $^3J_{H-H} = 7$ Hz, for the ethylene protons. The $^{31}P\{^1H\}$ NMR spectrum presents a sharp singlet at δ −13.02 for the phosphine groups.

Treatment of **1** with 3 equiv of $W(CO)_4(NCMe)_2$ in CH_2Cl_2 at ambient temperature produced a deep red solution, from which air-stable, dark red crystals of $N[CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2W(CO)_4]_3$ (**2**; 83%) were obtained by adding *n*-hexane.[19] The ^1H NMR spectrum shows that the imine N−CH resonance is shifted upfield to δ 8.08 upon coordination, and the $^{31}P\{^1H\}$ NMR spectrum displays the phosphine resonance at δ 24.62 concomitant with ^{183}W satellites ($J_{W-P} = 236$ Hz). The spectral data indicate equivalence of the three $[CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2W(CO)_4]$ units in solution, likely through C_3 rotations. The molecular structure of **2**, depicted in Figure 1, shows that each iminophosphino group chelates a $W(CO)_4$ moiety in a cis fashion. The central amine atom N4 is constrained 0.32 Å above the plane of three tungsten atoms, with nonbonding N4···W distances of 4.75−5.30 Å and W···W′ distances of 7.94−8.70 Å. The P−W−N bite angles are acute, being 79.7° on average, and the mean C=N length is 1.29 Å.

Compound **2** is thermally robust and shows little reactivity toward **1**, even at elevated temperatures. Thus, $W(CO)_3(NCMe)_3$ was prepared to react with **1** to afford $N[CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2W(CO)_3(NCMe)]_3$ (**3**) in 90% yield,[20] where each tungsten atom is linked to a labile acetonitrile ligand. Compound **3** forms a slightly air-sensitive, dark purple crystalline solid. The averaged CO stretching frequency at 1857 cm^{-1} for **3** is red-shifted by 60 cm^{-1} in comparison with **2** (average 1917 cm^{-1}), suggesting a stronger π-back-donation from the tungsten atom to the carbonyl ligands of **3**. The ^1H resonance for the imine protons (δ 7.82) and the ^{31}P resonance for the phosphine groups (δ 29.76 with $J_{W-P} = 225$ Hz) are comparable with those of **2**.

The reaction of **3** and **1** in CH_2Cl_2 took place at ambient temperature to produce air-stable, dark red crystals of $[N(CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2)_3]_2[W(CO)_3]_3$ (**4**) in 82% yield.[21] In contrast, attempts to synthesize **4** by self-assembly of **1** and $W(CO)_3(NCMe)_3$ in a 2:3 molar ratio led to a complex mixture. The ESI mass spectrum of **4** shows isotopically resolved peaks of the molecular ions in the range *m/z* 2726−2737. The IR spectrum in the carbonyl region displays a pattern in agreement with a *fac*-W(CO)$_3$LL′L″ configuration.[22] It appears that compound **4** exhibits an idealized C_3 symmetry in solution. Thus, the ^1H NMR spectrum (Figure 2A) shows a singlet at δ 8.62 for the free N−CH protons, a singlet at δ 7.94 for the coordinated N=CH protons, several multiplets at δ 8.05−5.51 for the phenyl protons, and eight signals from δ 3.57 to 1.57 for the CH_2 protons, which are diastereotopic due to asymmetric coordination of the ligands. Noticeably, a phenyl resonance at δ 5.51 is markedly shielded relative to the others and might

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[19] Anal. Calcd for $C_{75}H_{57}O_{12}N_4P_3W_3$: C, 48.67; H, 3.10; N, 3.03. Found: C, 48.66; H, 3.24; N, 3.09. MS (FAB): *m/z* 1850 (M^+, ^{184}W). IR (CH_2Cl_2, ν_{CO}): 2000 (m), 1898 (s), 1852 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 8.08 (s, 3H, N=CH), 7.58−7.34 (m, 39H, Ph), 6.83 (t, 3H, Ph), 3.75 (t, 6H, $^3J_{H-H} = 7$ Hz, CH_2), 2.45 (t, 6H, $^3J_{H-H} = 7$ Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 24.62 (s; with ^{183}W satellites $J_{W-P} = 236$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 210.8−202.3 (CO), 170.9 (N=CH), 138.4−128.7 (Ph), 72.5 (CH_2), 54.7 (CH_2). Crystal data for **2**: $M_r = 1850.71$, monoclinic, space group $P2_1/n$, $a = 20.5438(4)$ Å, $b = 9.0415(2)$ Å, $c = 38.2879(7)$ Å, $\beta = 101.1405(9)°$, $V = 6977.8(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.762$ g cm^{-3}, $\mu = 5.067$ mm^{-1}, $F(000) = 3592$, θ range 1.05−27.50°, 875 variables refined with 15 955 independent reflections to final *R* indices ($I > 2\sigma(I)$) of R1 = 0.0528 and wR2 = 0.1166, and GOF = 1.064.

[20] Anal. Calcd for for $C_{78}H_{66}N_7O_9P_3W_3$: C, 49.59; H, 3.52; N, 5.19. Found: C, 50.01; H, 3.86; N, 5.43. MS (FAB): *m/z* 1766 (M^+ − 3NCMe, ^{184}W). IR (CH_3CN, ν_{CO}): 1910 (s), 1792 (s) cm^{-1}. ^1H NMR (C_6D_6, 20 °C): δ 7.82 (s, 3H, N=CH), 7.41−6.71 (m, 42H, Ph), 3.56 (t, 6H, $^3J_{H-H} = 7$ Hz, CH_2), 2.45 (t, 6H, $^3J_{H-H} = 7$ Hz, CH_2), 2.02 (s, 9H, NCMe). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C): δ 29.76 (s; with ^{183}W satellites $J_{W-P} = 225$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 220.3−215.4 (CO), 170.4 (N=CH), 138.3−126.5 (Ph), 71.0 (CH_2), 56.4 (CH_2), 3.5 (CH_3).

[21] Anal. Calcd for $C_{135}H_{114}O_9N_8P_6W_3$: C, 59.40; H, 4.21; N, 4.10. Found: C, 59.87; H, 4.27; N, 4.02. MS (ESI): *m/z* 2728 (M^+, ^{184}W). IR (CH_2Cl_2, ν_{CO}): 1920 (s), 1808 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 20 °C): δ 8.62 (s, 3H, N=CH), 7.94 (s, 3H, W−N=CH), 8.05−6.63 (m, 81H, Ph), 5.51 (t, 3H, Ph), 3.57 (m, 3H, CH_2), 3.43 (m, 3H, CH_2), 3.30 (m, 3H, CH_2), 3.22 (m, 3H, CH_2), 2.76 (m, 3H, CH_2), 2.12 (m, 3H, CH_2), 2.02 (m, 3H, CH_2), 1.57 (m, 3H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 24.8 (d, $^2J_{P-P} = 24$ Hz; with ^{183}W satellites $J_{W-P} = 182$ Hz), 23.3 (d, $^2J_{P-P} = 24$ Hz; with ^{183}W satellites $J_{W-P} = 234$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 40 °C): δ 24.9 (s; with ^{183}W satellites $J_{W-P} = 220$ Hz). Crystal data for **4**: $M_r = 3260.38$, monoclinic, space group $C2/c$, $a = 33.3154(4)$ Å, $b = 36.4677(4)$ Å, $c = 28.8983(3)$ Å, $\beta = 124.3432(5)°$, $V = 28989.0(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.494$ g cm^{-3}, $\mu = 2.632$ mm^{-1}, $F(000) = 13\,168$, θ range 1.12−25.00°, 1578 variables refined with 25 474 independent reflections to final *R* indices ($I > 2\sigma(I)$) of R1 = 0.0731 and wR2 = 0.1898, and GOF = 1.015.

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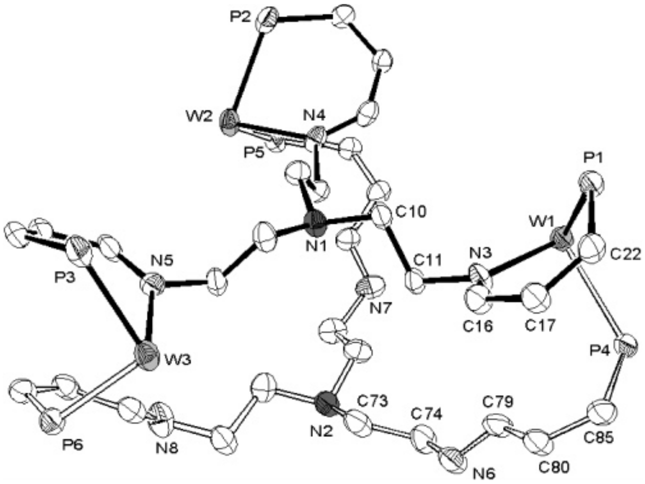

Figure 3. Simplified ORTEP diagram of **4**. Only the ring atoms are shown for clarity.

be attributed to the intramolecular aromatic contacts.[2] The variable-temperature $^{31}P\{^{1}H\}$ NMR spectra are shown in Figure 2B. At −60 °C, the two doublets at δ 24.8 and 23.3 ($^{2}J_{P-P}$ = 24 Hz), with both signals accompanied by ^{183}W satellites, are assigned to the phosphorus resonance for the η^2- and η^1-iminophosphino groups, respectively. The latter signal shows a downfield shift upon warming and becomes superimposed with the former at 40 °C, and the resulting singlet signal remains unchanged to 80 °C (taken in C_6D_6). Since the two N=CH proton resonances are retained in this temperature range, coincidence of the two phosphorus resonances is likely a result of accidental overlap but is not a dynamic equilibrium involving intramolecular η^1/η^2 site exchange of the iminophosphino groups.[23]

Recrystallization of **4** from CH_2Cl_2 by slow diffusion into diethyl ether afforded deep red crystals suitable for an X-ray diffraction study. The crystals of **4** contain a large number of solvent molecules, owing to the large cavities in the tricyclic, though rigid, molecules. The ORTEP diagram, showing only the ring atoms, is illustrated in Figure 3. The molecule consists of two $N(CH_2CH_2N{=}CH(o\text{-}C_6H_4)PPh_2)_3$ ligands bridged by three $W(CO)_3$ groups to form a metallatricyclic cage. The coordination about each tungsten atom is a distorted octahedron with three terminal carbonyls capping a triangular face. The iminophosphino linkages connected to the N1 atom are each chelating a tungsten atom, while those connected to the N2 atom are each bonded to a tungsten atom through the phosphine group. The arrangement of N1, N2, W1, W2, and W3 atoms can be viewed as a distorted trigonal biyramid, with the apical N1 and N2 atoms being 0.34 and 4.50 Å away from the W_3 plane, respectively. The nonbonding N1···W distances are in the range 4.97−5.24 Å (average 5.11 Å), while the N4···W distances are longer, being 6.76−6.92 Å with a mean value of 6.86 Å. The W···W′ distances are 8.82−9.14 Å (average 8.96 Å).

In summary, we have prepared the potentially heptadentate ligand **1**, which reacts with tungsten carbonyls to form the tripodal complexes **2** and **3**, and the tricyclic cage complex **4**. Although M_3L_2-type cages are relatively simple 3-D constructs, they remain uncommon.[24–26] We are currently investigating if metal cations can assemble a chain (or a circle) of **4** through interactions with the free amine atoms.

Acknowledgment. We are grateful for support of this work by the National Science Council of Taiwan.

Supporting Information Available: Complete crystallographic data of **2** and **4**; crystal data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050281P

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