

Figure 2. Molecular structure of $[\text{Ph}_3\text{PNH}_2][\text{OsN}(\eta^4\text{-HBA-B})]$ (**4**).

intensely colored purple product, **2**, together with a red as yet unidentified paramagnetic species. Complex **2** can be isolated following preparative TLC on silica gel plates in 30% yield. Recrystallization from ethanol/hexane affords small deep purple crystals. An X-ray analysis was performed.⁹ The X-ray structural study (Figure 1)¹⁰ reveals that the PAC ligand has isomerized to the *cis*- β geometry and a bidentate ligand has been produced. One plausible mechanism for the formation of the bidentate ligand involves the intermediacy of an Os(VIII) bis(imido) complex **3** (see Scheme I). Insertion of an imido nitrogen of **3** into the aryl C-H bond of the second imido ligand followed by proton migration would yield the bidentate ligand. Analogous reactions have been observed by Trogler et al. in photochemically initiated reactions of cobalt tetraazadiene complexes. High-valent diimido intermediates (cobalt(V)) were also invoked.¹¹ The identical ligand was found for the complex $[\text{HOs}_5(\text{CO})_{13}(\text{PhNC}_6\text{H}_4\text{NH})]$, obtained from the reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with azobenzene.¹²

- (9) ¹H NMR spectrum assigned following decoupling and NOE experiments. For assignments see Figure 1. ¹H NMR (CDCl_3), δ : 11.6 (s), N(3A)-H; 8.35 (dd), C(10A)-H; 8.05 (d), C(4C)-H; 7.3 (t), C-(6C)-H, C(6A)-H; 7.0 (m), C(7C)-H, C(7A)-H, C(11A)-H, C-(11C)-H, C(25A)-H, C(24A)-H, C(23A)-H; 6.92 (d), C(35A)-H; 6.8 (t), C(5C)-H, C(5A)-H; 6.48 (t), C(34A)-H; 6.35 (t), C(32A)-H; 6.28 (br t), C(33A)-H; 6.0 (d), C(26A)-H, C(22A)-H. Anal. Calcd for $\text{OsC}_{32}\text{H}_{22}\text{O}_4$: C, 53.62; H, 3.09; N, 7.82. Found: C, 53.49; H, 3.19; N, 7.65.
- (10) Structure determination of **2**: space group $P\bar{1}$, $Z = 4$, $\lambda = 0.7107 \text{ \AA}$, Enraf-Nonius CAD4 diffractometer, $a = 9.259(2) \text{ \AA}$, $b = 16.025(5) \text{ \AA}$, $c = 17.883(10) \text{ \AA}$, $\alpha = 95.37(4)^\circ$, $\beta = 94.49(4)^\circ$, $\gamma = 98.68(3)^\circ$, $V = 2600(2) \text{ \AA}^3$. Heavy-atom solution, full-matrix least-squares refinement on all coordinates and anisotropic Gaussian amplitudes of the non-hydrogen atoms minimizing $\sum w\Delta^2$, $w = \sigma_F^{-2}$, $\Delta = F_o^2 - (F_c/k)^2$, resulted in the goodness-of-fit $S = [\sum w\Delta^2/(n-v)]^{1/2} = 1.73$, $n = 8144$ reflections and $p = 739$ parameters (3 blocks, 246-247-246), $R_F = \sum ||F_o - |F_c|| / \sum |F_o| = 0.114$ (7143 reflections, $I > 0$), $R_F = 0.067$ (4378 reflections, $I > 3\sigma_I$). All calculations were carried out on a VAX 11/750 with the CRYM crystallographic system. The crystal of this compound was of poor diffracting quality so that counting rates and hence data precision were of low quality: the value of this determination lies principally in establishing the connectivity of the atoms. Additional details are given in the supplementary material.
- (11) (a) Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.* **1984**, *23*, 2968-2973. (b) Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.* **1980**, *209*, 407-414. (c) Gross, M. E.; Ibers, J. A.; Trogler, W. C. *Organometallics* **1982**, *1*, 503-535. (d) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 192-193.

Examples of this insertion reaction are also found in purely organic systems.¹³ Attempts are under way to trap the supposed Os(VIII) intermediate.

In contrast, reaction of **1** with 2 equiv of trimethylsilyl azide (*caution!*) in benzene at room temperature for 4 h yields the yellow nitrido complex **4**, which precipitates in pure form as the $[\text{Ph}_3\text{PNH}_2]^+$ salt (>90% yield).¹⁴ Recrystallization from CH_2Cl_2 affords X-ray-quality crystals.¹⁵ The results of an X-ray crystal structure determination are shown in Figure 2.¹⁶ The Os-N_{nitrido} bond distance (1.64 (1) Å) is consistent with an osmium-nitrogen triple bond.¹⁷ The osmium atom sits 0.56 Å above the PAC ligand plane with an average NML angle of 106.4°. Cation metathesis with $[\text{Et}_4\text{N}][\text{Cl}]$ gives the tetraethylammonium salt of the nitrido complex anion. When methyl azide (*caution!*) is passed through a solution of **1** in benzene, followed by workup with $[\text{Et}_4\text{N}][\text{Cl}]$, the same nitrido complex anion can be isolated in good yield (80%) as the tetraethylammonium salt.

Acknowledgment. We acknowledge the Rohm and Haas Co., the Atlantic Richfield Corp. of America, and the National Science Foundation (Grant CHE-84-06198) for generous support of this research. We thank Dr. Peter J. Desrosiers for helpful discussions and John T. Keech for assistance with NMR measurements. Upgrade of the Divisional X-ray Diffraction Facility was supported by the National Science Foundation (Grant CHE-82-19039).

Supplementary Material Available: Complete details of data collection and refinement and listings of bond distances and angles and of fractional atomic coordinates and Gaussian amplitudes (10 pages); listings of structure factor amplitudes (72 pages). Ordering information is given on any current masthead page.

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- (16) Structure determination of **4**: space group $P2_1/n$, Enraf-Nonius CAD4 diffractometer, $\lambda = 0.7107 \text{ \AA}$, $a = 9.555(2) \text{ \AA}$, $b = 23.675(3) \text{ \AA}$, $c = 14.375(3) \text{ \AA}$, $\beta = 93.26(2)^\circ$, $V = 3247(1) \text{ \AA}^3$, $Z = 4$; refinement and structure solution, as described above, led to $S = 1.75$ ($n = 5703$ reflections, $p = 433$ parameters), $R_F = 0.082$ ($n = 5153$ reflections, $I > 0$), $R_F = 0.049$ ($n = 3520$ reflections, $I > 3\sigma_I$). Additional details are given in the supplementary material.
- (17) Compare for example with the structure of $\text{K}_2[\text{OsNCl}_5]$ where the Os-N bond distance is 1.614 (13) Å: Bright, D.; Ibers, J. *Inorg. Chem.* **1969**, *8*, 709-715.
- (18) Contribution No. 7338.
- (19) Alfred P. Sloan Research Fellow, 1986-1988; Dreyfus Teacher-Scholar, 1986-1990.

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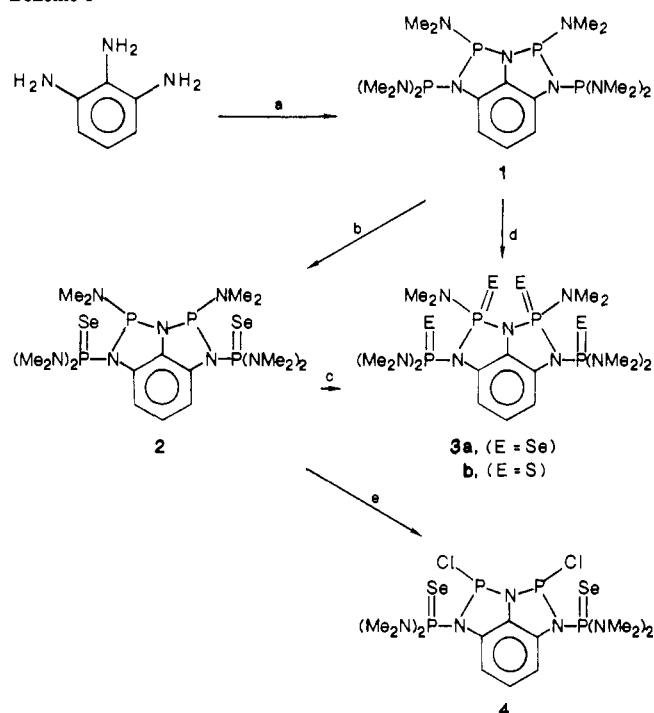
Received December 18, 1985

Syntheses of Stabilized Linear Tetraphosphazanes

Sir:

The development of linear P(III)-phosphazane chemistry has been severely limited by the absence of phosphazane $[(\text{PR}-\text{NR}')_n]$ members of significant ($n > 2$) chain extension.¹ This dearth occurs because reactions from which linear phosphazanes could

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Scheme 1^a

^a Reaction conditions: (a) $(\text{Me}_2\text{N})_3\text{P}/\text{Et}_2\text{NH}$, 70 °C, 36 h; (b) excess Se, CH_2Cl_2 , 25 °C, 20 h; (c) excess Se, CH_2Cl_2 , 40 °C, 3 days; (d) S_8 , CH_2Cl_2 , 25 °C, 12 h; (e) $\text{HCl}(\text{g})/\text{Et}_2\text{NH}_2\text{Cl}$, -196 °C, toluene, 1 h.

form result instead in four-,^{1,2} six-,^{1,3} or eight-membered^{1,4} ring products. Recently we undertook syntheses of P(III)-phosphazanes using template skeletal stabilization as a way to inhibit small-ring formation and promote linear product formation. We now wish to report preparation of the first skeletally stabilized linear tetraphosphazane, $\text{C}_6\text{H}_3\text{N}_3[\text{P}(\text{NMe}_2)_2]_2(\text{PNMe}_2)_2$ (**1**).

Reaction of 1,2,3- $(\text{NH}_2)_3\text{C}_6\text{H}_3$ with excess $(\text{Me}_2\text{N})_3\text{P}$ at 100 °C (Scheme I) results in formation of **1** (> 90% yield). Removal of the $(\text{Me}_2\text{N})_3\text{P}$ in vacuo yields **1** as an oil, which upon standing crystallizes to pure product (mp 62–66 °C).^{5,6} **1** reacts with 2 equiv of Se selectively at 25 °C to form diselenide **2**^{5,7} or with 4 equiv of Se at 40 °C to form the tetraselenide **3a**.^{5,8} Recrystallization of **2** from toluene or **3a** from CH_2Cl_2 yields pure **2** (mp 91–94 °C) or **3a**· CH_2Cl_2 (mp 254–258 °C), respectively. Sulfur reacts with **1** in toluene directly to give the tetrasulfide **3b**,^{5,9} showing no apparent selective oxidation of phosphorus atoms.

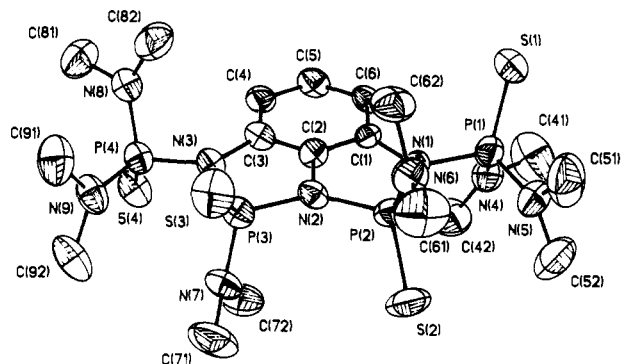


Figure 1. Structure and numbering scheme for $\text{C}_6\text{H}_3\text{N}_3[\text{PS}(\text{NMe}_2)_2]_2 \cdot [\text{P}(\text{NMe}_2)_2]_2$ (**3b**) showing 50% probability thermal ellipsoids. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)–N(1), 1.696 (5); P(4)–N(3), 1.699 (5); P(2)–N(1), 1.772 (5); P(3)–N(3), 1.734 (5); P(2)–N(2), 1.707 (5); P(3)–N(2), 1.695 (5); C(1)–N(1), 1.438 (7); C(2)–N(2), 1.390 (7); C(3)–N(3), 1.448 (7); P=S(mean), 1.921 (3); N(1)–P(2)–N(2), 91.7 (2); N(2)–P(3)–N(3), 91.2 (2); P(2)–N(2)–C(2), 110.3 (4); P(3)–N(2)–C(2), 111.5 (4); C(1)–N(1)–P(2), 111.9 (4); C(3)–N(3)–P(3), 111.7 (4); P(2)–N(2)–P(3), 138.2 (3); C(2)–C(1)–N(1), 109.2 (5); C(2)–C(3)–N(3), 109.2 (5); N(2)–C(2)–C(1), 116.8 (5); N(2)–C(2)–C(3), 116.5 (5); C(1)–C(2)–C(3), 126.7 (6).

The tetrasulfide (**3b**) and tetraselenide (**3a**) crystallize from CH_2Cl_2 as monosolvates, **3a,b**· CH_2Cl_2 .

The new tetraphosphazanes are surprisingly stable. **1** shows no decomposition after 10 days in air at ambient temperatures; **2**, **3a**, and **3b** showed no decomposition during 2 weeks. Hydrogen chloride reacts rapidly and indiscriminately with **1**; however, with **2** reaction occurs below room temperature to form the dichloride **4** selectively. Recrystallization from toluene yields pure **4** (>80% yield, mp 125 °C dec).^{5,10}

Compounds **3a**· CH_2Cl_2 and **3b**· CH_2Cl_2 are isomorphous; the structure of the latter has been solved completely by single-crystal X-ray analysis.¹¹ **3b**· CH_2Cl_2 contains eight molecules per unit cell. **3b** is a $(\text{Me}_2\text{N})_2\text{P}$ -substituted tricyclic benzobis(phosphadiazole) (Figure 1), in which a P_4N_3 tetraphosphazane unit is stabilized by bonding of the three skeletal nitrogen atoms to the 1,2,3-positions of the benzene ring. **3a** has approximate C_2 point group symmetry, with the C_2 axis colinear with the N(2)–C(2)–C(5) vector. The endo P=S bonds P(2)–S(2) and P(3)–S(3) are oriented trans to one another and, in the solid, trans to the exo P=S groups. The $(\text{Me}_2\text{N})_2\text{P}$ units bridge arene ring nitrogens N(1)/N(2) and N(2)/N(3) without "dishing" of the molecule. The P_4N_3 skeleton and C_6 ring are within experimental error coplanar. Some bond distance and angle distortions occur to maintain the planar geometry. The mean $\angle\text{C}(4)\text{--C}(3)\text{--N}(3)$ and $\angle\text{C}(6)\text{--C}(1)\text{--N}(1)$ of 133.5° and the P(2)–N(2)–P(3) angle of 138.2° are unusually large. The C(3)–N(3) and C(1)–N(1) bonds (mean 1.443 Å) are longer than the inner C(2)–N(2) bond

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- (5) Satisfactory elemental analyses were obtained for all compounds.
- (6) **1**: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ 110.6 [area 2, P(2), P(3)], 109.2 [area 2, P(1), P(4)], complex, $^2J_{\text{P}(2)\text{P}(3)}$ = 70.4 Hz, $^2J_{\text{P}(1)\text{P}(2)}$ = 66.4 Hz; ^1H NMR (C_6D_6) δ 6.78 (m, area 3, Ph), 2.59 [d, area 24, CH_3 (exo)], 2.40 [d, area 12, CH_3 (ring)]; MS, parent at m/e 505, $\text{C}_{18}\text{H}_{39}\text{N}_9\text{P}_4$.
- (7) **2**: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ 120.6 [area 2, P(2), P(3)], 75.0 [area 2, P(1), P(4)], complex $^2J_{\text{P}(2)\text{P}(3)}$ = 82.0 Hz, $^2J_{\text{P}(1)\text{P}(2)}$ = 70.7 Hz, $^4J_{\text{P}(1)\text{P}(3)}$ = -2.2 Hz; ^1H NMR (C_6H_6) δ 6.98–6.77 (complex, area 3, Ph), 2.52 (m, area 36, CH_3).
- (8) **3a**: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ 59.0 [area 2, P(2), P(3)], 52.1 [area 2, P(1), P(4)], complex, $^2J_{\text{P}(2)\text{P}(3)}$ = 11.0 Hz, $^2J_{\text{P}(1)\text{P}(2)}$ = 15.5 Hz, $^4J_{\text{P}(1)\text{P}(3)}$ = -2.1 Hz; ^1H NMR (C_6D_6) δ 7.08–6.89 (complex, area 3, Ph), 2.50–2.11 (complex, area 24, CH_3).

- (9) **3b**: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ 60.6 [area 2, P(2), P(3)], 60.1 [area 2, P(1), P(4)], complex, $^2J_{\text{P}(2)\text{P}(3)}$ = 11.0 Hz, $^2J_{\text{P}(1)\text{P}(2)}$ = 18.2 Hz; ^1H NMR (C_6D_6) δ 6.82 (m, area 3, Ph), 2.85 [m, area 24, CH_3 (exo)], 2.74 [m, area 12, CH_3 (ring)]; MS (FAB, glycerol/ CH_2Cl_2 matrix), parent at m/e 634, $\text{C}_{18}\text{H}_{39}\text{N}_9\text{P}_4\text{S}_4$.
- (10) **4**: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ 147.2 [d, area 2, $^2J_{\text{PP}}$ = 71.3 Hz, P(2), P(3)], 65.5 [d, area 1, P(1), P(4)]; ^1H NMR (C_6D_6) δ 7.08–6.89 (complex m, area 3, Ph), 2.50–2.11 (complex m, area 24, CH_3).
- (11) Crystal data for $\text{C}_{18}\text{H}_{39}\text{N}_9\text{P}_4\text{S}_4 \cdot \text{CH}_2\text{Cl}_2$: formula weight 718.65, orthorhombic, $Pbca$, $a = 14.706$ (3) Å, $b = 21.610$ (5) Å, $c = 22.000$ (5) Å, $V = 6991$ (3) Å³, $Z = 8$, $d_{\text{obsd}} = 1.18$ g/cm³, $d_{\text{calcd}} = 1.20$ g/cm³. Intensity data: Nicolet P3/F autodiffractometer, Mo K_α ($\lambda = 0.71069$ Å), θ - 2θ scan mode, $3.0 < 2\theta < 50.0$, 7117 reflections collected (6182 unique), of which 2390 were observed [$(F_o) > 6\sigma(F_o)$]. The data were corrected for a 34% decline in intensity. An empirical absorption correction was applied. The structure was solved by direct methods and refined by block-cascade least-squares calculations; $R = 0.049$, $R_w = 0.050$. For the final refinement, the thermal parameters for the solvent molecule and the phosphorus, sulfur, and nitrogen atoms were treated anisotropically; those of carbon were treated isotropically. Hydrogen atoms were included in idealized geometries, riding on the atoms to which they are attached, with a single refined isotropic thermal parameter.

(1.390 Å), and the P(2)-N(1) and P(3)-N(3) distances (mean 1.728 Å) are longer than the inner P(2)-N(2) and P(3)-N(2) distances (mean 1.701 Å). The P(2)-N(1) and P(3)-N(3) bonds are relatively long for typical phosphazane P-N bonds (eg. 1.65-1.70 Å)^{1,2,4c,e} however, the other P-N distances in **3b** are as expected.

The tetraphosphazanes **1-4** are characterized by a combination of ¹H and ³¹P NMR, IR, and mass spectral data. All show basic AA'XX' or AA'BB' ³¹P NMR spectral patterns,¹² analogous to that of **3b** and consistent with the presence of only one isomer. Hence all series members are inferred to be structurally analogous to **3b**, i.e. trans bonded around the central P(2)-N(2)-P(3) linkage. The ²J_{P(2)P(3)} coupling constant of 70.4 Hz in **1** is consistent with those seen in *trans*-diphosphinoamines reported previously.¹³ The outer P-N-P couplings, ²J_{P(1)P(2)} and ²J_{P(3)P(4)}, are slightly smaller and assumed to be the average of all possible conformations around the exo P-N bonds. Similar comparison data for the λ⁴-λ³ (**2** or **4**) or the λ⁴-λ⁴ compound (**3a** and **3b**) are not available; however, it is of interest to note that ²J_{P(2)P(3)} values in **3** and **4** are smaller than that observed in **1**.

Compound **1** is a unique example of a molecule containing a diphosphinoamine unit [P(2)-N(2)-P(3)] stereoselectively formed as the *trans d,l* isomer. Although reaction of PhPCl₂ with *i*-PrNH₂ yields *meso-i*-PrN[PhP(*i*-PrNH)]₂ diastereomerically selectively,¹⁴ such selectivity has not been recognized generally in diphosphinoamine formation reactions. How formation of **1** as one diastereomer results and is a function of the skeletal stabilization in the system is of interest. Perhaps with substituent modifications, such reactions can be used in other stereoisomeric selective syntheses.

The successful attachment of a tetraphosphazane unit to three adjacent positions on a benzene ring without major distortion of the systems or loss of planarity suggests that it might be possible to extend the phosphazane skeleton to completely encircle the C₆ ring with an (RPN)₆ "supercycle" azane ring. Such molecules and their derivatives might have novel magnetic and/or electronic properties analogous to those reported recently by Breslow and co-workers.¹⁵

Acknowledgment. Support for this work by National Science Foundation Grant CHE-8312856 is gratefully acknowledged.

Supplementary Material Available: Listings of the crystal structure determination and crystal structure data, positional parameters, anisotropic thermal parameters, bond distances, and bond angles (8 pages). Ordering information is given on any current masthead page.

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Received July 31, 1986

Resonance Raman Spectra of Charge-Transfer Excited States of Copper(I) Complexes

Sir:

Resonance Raman spectroscopy is now well-established¹ as an important probe of the charge-transfer excited states of metal

complexes and in particular as an effective way of investigating the extent of localization of the excited electron on acceptor ligand orbitals.² With one exception,³ previous work has focused attention on the excited states of d⁶ metal ion complexes. We wish here to report the first examples of resonant Raman scattering from the excited states of some photoelectrochemically interesting⁴ d¹⁰ systems, namely the metal-ligand charge-transfer (MLCT) states of the four-coordinate copper(I) complexes [Cu(DPP)₂]⁺ and [Cu(DMP)(Ph₃P)₂]⁺ (DPP and DMP are respectively 2,9-diphenyl- and 2,9-dimethyl-1,10-phenanthroline), for which we have recently measured⁵ excited-state absorption spectra. The results provide convincing evidence that in the MLCT excited state of [Cu(DPP)₂]⁺, the transferred electron is localized on one ligand. Our findings suggest that localized excitation, originally demonstrated for the CT excited states of a variety of Ru(II) complexes,² is a rather general phenomenon among the MLCT excited states of transition-metal systems.

The resonance Raman studies were carried out at the Laser Support Facility of the U.K. Science and Engineering Research Council (Rutherford Appleton Laboratory). Ground-state spectra were generated by means of an Ar⁺ laser (Innova 90) at wavelengths of 363.8 and 488 nm. An excimer-pumped dye laser (Lambda Physik FL2002E) was used for the excited-state investigations. In all cases, the excited-state lifetimes were sufficiently long in comparison with the laser pulse duration (10 ns) and the extent of overlap of the ground- and excited-state absorption spectra of the complexes was such that the same laser pulse served both to populate and to interrogate the excited species. The complexes were prepared by literature methods.^{4b,c} Argon-purged solutions in methanol (ca. 10⁻³ mol dm⁻³) were flowed through quartz capillary sample tubes, and the laser beam was brought to a focus just beyond the irradiated zone. Raman scattered radiation, dispersed through a Spex Triplemate spectrograph (1200 lines/mm grating), was detected by an intensified diode array (EG&G, Model 1420). Raman spectra of indene and cyclohexane, recorded under the same experimental conditions as the complex spectra, were used for calibration purposes. Spectra recorded on several different visits to the Laser Centre were very reproducible, and the peak positions in the spectra reported here are reliable to better than 4 cm⁻¹.

As a strategy for establishing the nature of the MLCT excited states of the bis(ligand) complex, resonance Raman spectra of [Cu(DPP)₂]⁺ were compared with those of the mixed-ligand species [Cu(DMP)(Ph₃P)₂]⁺. The latter complex has^{4c} an intense MLCT (Cu→DMP) band in the region of 360 nm, and the charge-transfer state populated by excitation in this spectral region necessarily has the excited electron localized on the single DMP ligand. The photoexcited complex is thus in effect a source of the disubstituted 1,10-phenanthroline radical anion.⁶ Figure 1a shows the excited-state absorption spectrum, with UV and visible bands resembling the published⁷ absorption spectra of the radical anions of 1,10-phenanthroline and related N-heteroaromatic

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