**Table II.** NMR Data for New Compounds[a]

| | |
|---|---|
| **1a** | 7.1–7.8 (m, $C_6H_5$) |
| **1b** | 7.7 (m, $C_6H_5$), 7.01 (d, 2, $^3J_{HH} = 8.1$, $C_6H_4$), 6.82 (d, 2, $^3J_{HH} = 8.1$, $C_6H_4$), 2.26 (s, 3, $CH_3$) |
| **1c** | 7.45 (m, $C_6H_5$), 9.89 (s, 1, $CHO$), 7.71 (d, 2, $^3J_{HH} = 7.5$, $C_6H_4$),[b] 6.98 (d, 2, $^3J_{HH} = 7.2$, $C_6H_4$) |
| **1d** | 7.5 (m, $C_6H_5$), 1.84 (p, 1, $^3J_{HH} = 6.6$, $CHEt_2$), 1.14 (dq, 4, $^3J_{HH} = 6.6$ and 7.4, $CH_2$), 0.60 (t, 6, $^3J_{HH} = 7.4$, $CH_3$) |
| **2a** | 7.5 (m, $C_6H_5$), 7.24 (d, $J = 7.1$)[b], 7.18, 7.15 (d, $J = 3.4$), 7.05 (t, $J = 5.8$), 7.00 (m), 6.97 (dd, $J = 5.1$ and 7.3) |
| **2b** | 7.5 (m, $C_6H_5$), 7.14 (dd, 4, $^3J_{HP} = 9.8$, $^3J_{HH} = 6.0$, $C_6H_4$), 6.95 (dd, 4, $^3J_{HP} = 10.0$, $^3J_{HH} = 6.0$, $C_6H_4$), 6.44 (d, 4, $^3J_{HH} = 6.5$, $C_6H_4$), 6.29 (d, 4, $^3J_{HH} = 6.2$, $C_6H_4$), 2.93 (S, 12, $CH_3$), 2.92 (s, 12, $CH_3$) |
| **2c** | 7.55 (d, 12, $^3J_{HH} = 8.1$, $AsC_6H_4$), 7.36, 7.21 (m, 4, $P(C_6H_5)_2$), 7.15 (d, 12, $^3J_{HH} = 7.8$, $AsC_6H_4$), 6.99, 6.94 (m, 4, $P(C_6H_5)_2$), 2.3 (s, 18, $CH_3$) |

[a] Measured at 25 °C in $CDCl_3$; all chemical shifts ($\delta$) are given in ppm with respect to internal TMS, and coupling constants are given in Hz. [b] Some peaks obscured by the triphenylphosphine multiplet.

modes for the phosphinate bridges are split, and two bands are seen for the asymmetric and symmetric modes, which probably originates from solid-state crystal splitting. The splitting in **2b** was obscured by the broadness of these bands.

## Conclusion

The preparations described here represent a convenient, and probably general, entry into dimers of Ru(I) and possibly Os(I). The formation of **1c** has shown that reactive groups on the bridging ligand can easily be introduced. The hitherto unknown phosphinate dimers are a new class of reactive compounds. The dimers may be good starting materials for other M(I) complexes, the chemistry of which is at present very poorly understood in comparison to that of the M(II) and M(0) oxidation states.[2,14]

## Experimental Section

The reactions described were performed under nitrogen with standard Schlenk techniques. However the air-stable products were recrystallized under open conditions by slow evaporation of the specified solvent pairs.

**$[Ru_2(O_2CPh)_2(CO)_4(PPh_3)_2]$ (1a).** $Ru_3(CO)_{12}$, (0.1 g, 0.16 mmol) and an excess of benzoic acid (0.096 g, 1.27 mmol) were heated under nitrogen in 20 mL of THF for 2 h. The mixture was briefly cooled, triphenylphosphine (0.12 g, 0.46 mmol) was added, and the resultant mixture was heated at reflux for a further 30 min. The resulting bright yellow solution was cooled, THF was removed in vacuo, and the yellow oil was recrystallized from dichloromethane/ethanol to give 0.165 g, 65%, of **1a** as yellow cubes, mp 267–275 °C. Anal. Calcd for $C_{54}H_{40}O_8P_2Ru_2\cdot{}^1/_2CH_2Cl_2$: C, 58.23; H, 3.68. Found: C, 57.76; H, 3.56. The presence of dichloromethane solvate was confirmed by $^1H$ NMR spectroscopy.

**$[Ru_2(O_2C\text{-}p\text{-}tolyl)_2(CO)_4(PPh_3)_2]$ (1b). From $Ru_3(CO)_{12}$.** Compound **1b** was prepared in 63% yield as described for **1a**; mp 257–258 °C. Anal. Calcd for $C_{56}H_{44}O_8P_2Ru_2\cdot{}^1/_4CH_2Cl_2$: C, 59.77; H, 3.98. Found: C, 59.43; H, 3.34. The presence of dichloromethane solvate was confirmed by $^1H$ NMR spectroscopy.

**From $Ru_3(CO)_9(PPh_3)_3$.** $Ru_3(CO)_9(PPh_3)_3$ (0.05 g, 0.04 mmol) and 3 mL (ca. 25 mmol) of freshly distilled 4-methylbenzaldehyde were heated at 105 °C for 2 h, during which time the purple solution became a yellow oil. The mixture was then cooled, and the volatile materials were stripped off in vacuo. Recrystallization from dichloromethane/ethanol returned 0.04 g, 65%, of **1b**.

**$[Ru_2\{O_2CC_6H_4CHO\}_2(CO)_4(PPh_3)_2]$ (1c).** $Ru_3(CO)_{12}$ (0.078 g, 0.12 mmol) and an excess of 2-carboxybenzaldehyde (0.108 g, 0.72 mmol) were heated at reflux for 4 h. Triphenylphosphine (0.12 g, 0.46 mmol) was then added and the reaction mixture heated a further 20 min. Recrystallization from dichloromethane/ethanol returned 0.12 g, 59%, of yellow cubes, mp 216–220 °C. Anal. Calcd for $C_{56}H_{40}O_{10}P_2Ru_2\cdot{}^1/_2CH_2Cl_2$: C, 57.53; H, 3.51. Found: C, 57.96; H, 3.69. The presence of dichloromethane solvate was confirmed by $^1H$ NMR spectroscopy.

**$[Ru_2(O_2CCHEt_2)_2(CO)_4(PPh_3)_2]$ (1d). From $Ru_3(CO)_{12}$ and 2-Ethylbutyric Acid.** Compound **1d** was prepared as above from $Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol), excess 2-ethylbutyric acid (1 mL, ca. 8 mmol), and triphenylphosphine (0.12 g, 0.46 mmol). Recrystallization yielded 0.65 g, 86%, of yellow cubes, mp 206–208 °C. Anal. Calcd for $C_{52}H_{52}O_8P_2Ru_2$: C, 58.41; H, 4.91. Found: C, 58.35; H, 4.74.

**From $Ru_3(CO)_{12}$ and 2-Ethylbutyraldehyde.** $Ru_3(CO)_{12}$ (0.075 g, 0.12 mmol) and 3 mL (ca. 25 mmol) of freshly distilled 2-ethylbutyraldehyde were heated at reflux, 117 °C, for 4 h. The resulting red solution was cooled and stripped to dryness in vacuo. Triphenylphosphine (0.092 g, 0.35 mmol) and 20 mL of ethanol were then added. The resulting yellow suspension was heated at reflux for an additional hour, cooled, and filtered. The solid was then washed with ethanol and *n*-hexane, to give 0.153 g, 85%, of **1d**.

**From $Ru_3(CO)_9(PPh_3)_3$.** $Ru_3(CO)_9(PPh_3)_3$ (0.056 g, 0.04 mmol) and 2 mL (ca. 15 mmol) of freshly distilled 2-ethylbutyraldehyde were heated at reflux for 1 h, during which time the purple suspension became a yellow oil. The mixture was then cooled, and the volatile materials were stripped off in vacuo. Recrystallization from dichloromethane/ethanol returned 0.039 g, 60%, of **1d**.

**$[Ru_2(O_2PPh_2)_2(CO)_4(PPh_3)_2]$ (2a).** $Ru_3(CO)_{12}$ (0.06 g, 0.09 mmol) and diphenylphosphinic acid (0.123 g, 0.56 mmol) were heated at reflux for 14 h. The solution was then briefly cooled, triphenylphosphine (0.065 g, 0.24 mmol) was added, and this mixture was heated at reflux for an additional hour. The resulting yellow solution was cooled, and THF was removed in vacuo. Recrystallization of the oily residue from dichloromethane/ethanol returned 0.122 g, 68%, of **2a**, mp 244–246 °C. Anal. Calcd for $C_{64}H_{50}O_8P_4Ru_2$: C, 60.38; H, 3.96. Found: C, 59.80; H, 3.92.

**$[Ru_2\{O_2P(p\text{-}Me_2NC_6H_4)_2\}_2(CO)_4(PPh_3)_2]$ (2b).** $Ru_3(CO)_{12}$ (0.043 g, 0.07 mmol), bis(*p*-(dimethylamino)phenyl)phosphinic acid (0.123 g, 0.40 mmol), and triphenylphosphine (0.293 g, 1.12 mmol) were utilized as described above for **2a**. Yellow crystals (0.11 g, 75%; mp 236–242 °C) were obtained after recrystallization from dichloromethane/ethanol. Anal. Calcd for $C_{72}H_{70}N_4O_8P_4Ru_2$: C, 59.63; H, 4.83; N, 3.88. Found: C, 59.83; H, 4.88; N, 3.68.

**$[Ru_2(O_2PPh_2)_2(CO)_4\{As(p\text{-}tolyl)_3\}_2]$ (2c).** This preparation is identical with that of **2a** except that 0.131 g (0.38 mmol) of tri-*p*-tolylarsine was added instead of triphenylphosphine. Workup as for **2a** returned 0.13 g, 64%, of yellow crystals, mp 240–248 °C. Anal. Calcd for $C_{70}H_{62}As_2O_8P_2Ru_2$: C, 58.18; H, 4.32. Found: C, 57.78; H, 4.27.

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# Synthesis and Structure of the Trinuclear Palladium Cluster $[Pd_3(PEt_3)_3(\mu_2\text{-}NPh)_2(\mu_2\text{-}NHPh)]Cl$, Containing Bridging Imido and Amido Ligands

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The chemistry of nitrene or imido ligands[1] coordinated to electron-rich metals has been little developed, whereas much is known about the chemistry of such ligands coordinated to electron-deficient early transition metals.[2] Such species are of possible importance as intermediates in metal-catalyzed reductions of nitroaromatics.[3] We recently used the tetrazenido dianion, I, $[RNN{=}NNR]^{2-}$, to synthesize main-group and transition-metal metallacyclotetrazene complexes.[4] Although palladium is the

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**Table I.** Crystallographic Data for $[Pd_3(PEt_3)_3(\mu_2\text{-}NPh)_2(\mu_2\text{-}NHPh)]Cl$

| | |
|---|---|
| chem formula: $C_{36}H_{61}N_3P_3ClPd_3$ | fw = 983.5 |
| space group: $P\bar{1}$ | $T$ = 23 °C |
| $a$ = 11.567 (4) Å | $Z$ = 2 |
| $b$ = 12.877 (4) Å | $\lambda$ = 0.71073 Å |
| $c$ = 16.763 (7) Å | $\mu$ = 13.77 $cm^{-1}$ |
| $\alpha$ = 110.47 (3)° | $2\theta$ range: 3–45° |
| $\beta$ = 98.06 (3)° | $R$ = 0.058 |
| $\gamma$ = 105.77 (3)° | $R_w$ = 0.074 |
| $V$ = 2172.9 $Å^3$ | $F(000)$ = 996.0 |

primary metal used in homogeneously catalyzed reductive carbonylation of nitroaromatics, there are few examples of imido or amido complexes with this metal. Herein we report an example where both ligands are represented within a palladium cluster framework and derived from a ligand related to I.

## Experimental Section

Reactions were performed with standard Schlenk and cannula filtration techniques using a nitrogen atmosphere. Solids were manipulated under nitrogen in a Vacuum Atmospheres glovebox equipped with an HE-493 recirculator. Glassware was flame-dried before use. Pentanes were distilled from sodium, and tetrahydrofuran and benzene were distilled from potassium benzophenone ketyl. Phenyl azide,[5] $NiCl_2(PPh_2Me)_2$,[6] $PdCl_2(PEt_3)_2$,[6] and $PtCl_2(PEt_3)_2$[6] were prepared by literature methods (*Caution! Phenyl azide is explosive; exposure to acid or heavy metals should be avoided.*) The phenyl azide was stored and used as a 2–3 M toluene solution. Ethylenediamine was purified by a literature method.[7a] $^{31}P$ and $^1H$ NMR spectra were recorded with use of a General Electric-QE 300-MHz spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

**Synthesis of $[Li(THF)_x]_2[PhN_3NHCH_2CH_2NH]$ (II).** A slurry of $LiNHCH_2CH_2NH_2$ was prepared by adding 4.8 mL of 1.6 M *n*-BuLi (7.68 mmol) in hexane to 0.5 mL (7.47 mmol) of $NH_2CH_2CH_2NH_2$ in 30 mL of THF under $N_2$. To this light yellow slurry was added 3.5 mL (7.7 mmol) of 2.2 M $PhN_3$ dissolved in toluene to give a dark red solution. After 20 min, an additional 15 mL (24.0 mmol) of *n*-BuLi was added slowly and a yellow solid formed. After 1.5 h, the slurry was concentrated to 15 mL and 60 mL of pentane was added to give 1.1 g of a yellow precipitate. The yellow slurry of $[Li(THF)_x]_2[PhN_3NHCH_2CH_2NH]$ was filtered and dried under vacuum. Complex II is air and moisture sensitive and exhibits a slight solubility in THF and benzene. Unfortunately, we could not fully characterize II. For example, addition of a proton source to II in deuterated methanol generates $PhND_2$, $N_2$, and ethylenediamine. Elemental analyses were not reproducible because of the variation in the amount of coordinated THF molecules, which depends on the duration of vacuum-drying and the experimental scale. Therefore, the structure of reagent II is tentative. It can, however, be prepared reproducibly and used in the synthesis of a novel nitrene cluster.

**Synthesis of $[Pd_3(PEt_3)_3(\mu_2\text{-}NPh)_2(\mu_2\text{-}NHPh)]Cl$ (III).** Addition of 0.2 g of II in 20 mL of benzene to a stirred yellow solution of 0.3 g (0.73 mmol) of $PdCl_2(PEt_3)_2$ gave a dark red solution after 18 h. This solution was filtered, concentrated, and layered with pentane to yield (0.037 g, 18%) of dark red crystals of $[Pd_3(PEt_3)_3(\mu_2\text{-}NPh)_2(\mu_2\text{-}NHPh)]Cl$ (III). The isolated compound is insoluble in most solvents, with a slight solubility in acetone and DMSO. $^{31}P$ NMR (acetone-$d_6$): $\delta$ −0.90 (br). Anal. Calcd for $C_{36}H_{61}N_3P_3ClPd_3$: C, 43.97; H, 6.25. Found: C, 43.39; H, 6.09.

**Structure Determination of $[Pd_3(PEt_3)_3(\mu_2\text{-}NPh)_2(\mu_2\text{-}NHPh)]Cl$.** X-ray data were collected with use of a Nicolet R3m/V automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table I. The orientation matrix and unit cell parameters were determined from 20 machine-centered reflections with $15 < 2\theta < 30°$. Intensities of three check reflections were monitored after every 100 reflections during data collection. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. All calculations were carried out on a Microvax II computer with use of the SHELXTL PLUS program.

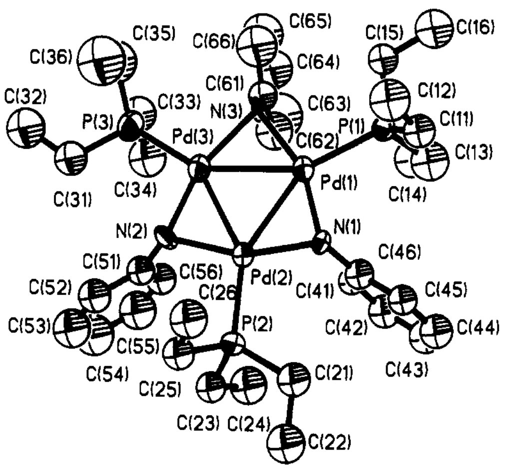
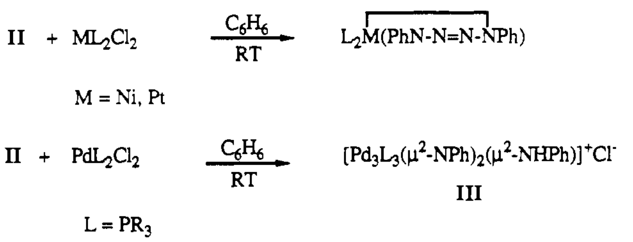
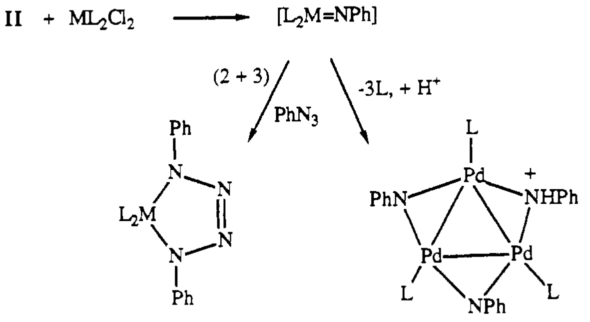


Figure 1. Thermal ellipsoid plot of the $[Pd_3(PEt_3)_3(\mu_2\text{-}NPh)_2(\mu_2\text{-}NHPh)]^+$ cation at the 50% probability level.

**Scheme I**



**Scheme II**



A dark red crystal of III, shaped as a block, of approximate dimensions 0.2 × 0.3 × 0.4 mm, was used for crystal and intensity data collection. Unit cell parameters suggested a triclinic lattice. The structure was solved by direct methods, and successful convergence was obtained in the centrosymmetric space group $P\bar{1}$ for 3422 unique reflections ($F_o > 8\sigma(F_o)$). Palladium and phosphorus atoms were refined anisotropically, and the phenyl groups were treated as isotropic rigid groups with fixed hydrogens (0.09 $Å^2$ fixed isotropic thermal parameter). One disordered phenyl ring (C(61)–C(66)) refined between two sites of 0.7 and 0.3 occupancy. The largest peak in the final difference Fourier map was 1.0 e/$Å^3$. Of 5641 unique reflections, 2219 with $I > 4\sigma(I)$ were used in the refinement of 198 least-squares variables. Final atomic positional and isotropic thermal parameters are given in Table II. Selected bond distances and bond angles are given in Table III.

## Discussion

The dianionic reagent $[Li(THF)_x]_2[PhNN{=}NNHCH_2CH_2NH]$ (II) was prepared from ethylenediamine, through deprotonation, N–N coupling, and deprotonation. The reaction between II and $NiCl_2(PPh_2Me)_2$ and *cis*-$PtCl_2(PEt_3)_2$ gave known cyclic metal–tetrazene complexes, $Ni(1,4\text{-}Ph_2N_4)(PPh_2Me)_2$ and $Pt(1,4\text{-}Ph_2N_4)(PEt_3)_2$ (Scheme I), as identified by comparison of their spectral and unit cell parameters with those we previously reported.[4] On the other hand, addition of II to *cis*-$PdCl_2(PEt_3)_2$ produced a trinuclear palladium cluster, $[Pd_3(PEt_3)_3(\mu_2\text{-}NPh)_2(\mu_2\text{-}NHPh)]Cl$ (III). This contrasts with the use of I, which fails to produce III even if ethylenediamine is added to the reaction mixture. Although we could not trap II, it presumably undergoes fragmentation (Scheme II) to donate an

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**Table II.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

| | *x* | *y* | *z* | *U*(eq),[a] $Å^2$ |
|---|---|---|---|---|
| Pd(1) | −746 (2) | 6160 (1) | 2871 (1) | 43 (1) |
| Pd(2) | 898 (2) | 5270 (1) | 3435 (1) | 38 (1) |
| Pd(3) | −1230 (2) | 3770 (1) | 2207 (1) | 49 (1) |
| P(1) | −1296 (5) | 7786 (5) | 3050 (4) | 48 (3) |
| C(11) | −1114 (21) | 8708 (20) | 4170 (15) | 61 (7) |
| C(12) | −1906 (28) | 8105 (26) | 4607 (20) | 97 (9) |
| C(13) | −299 (29) | 8844 (29) | 2706 (22) | 104 (10) |
| C(14) | −372 (28) | 8328 (27) | 1747 (21) | 98 (9) |
| C(15) | −2900 (21) | 7457 (20) | 2483 (15) | 60 (7) |
| C(16) | −3355 (28) | 8496 (26) | 2742 (20) | 98 (9) |
| P(2) | 2750 (5) | 5522 (5) | 4282 (4) | 44 (3) |
| C(21) | 3699 (23) | 7031 (21) | 5031 (16) | 67 (7) |
| C(22) | 4956 (26) | 7176 (25) | 5606 (18) | 86 (9) |
| C(23) | 3819 (21) | 4989 (20) | 3663 (15) | 61 (7) |
| C(24) | 4142 (28) | 5628 (27) | 3050 (20) | 98 (9) |
| C(25) | 2566 (21) | 4685 (19) | 4973 (15) | 58 (6) |
| C(26) | 1738 (25) | 4978 (23) | 5554 (18) | 79 (8) |
| P(3) | −2538 (6) | 1887 (5) | 1315 (5) | 66 (3) |
| C(31) | −2071 (24) | 724 (23) | 1431 (17) | 74 (8) |
| C(32) | −2982 (31) | −550 (29) | 848 (21) | 111 (11) |
| C(33) | −2816 (28) | 1580 (25) | 120 (19) | 90 (9) |
| C(34) | −1715 (33) | 1747 (31) | −180 (23) | 120 (12) |
| C(35) | −4087 (33) | 1508 (31) | 1469 (25) | 126 (12) |
| C(36) | −4133 (40) | 1536 (38) | 2318 (30) | 159 (15) |
| N(1) | 947 (14) | 6943 (14) | 3774 (10) | 38 (4) |
| C(41) | 2171 (14) | 7523 (11) | 2816 (8) | 50 (6) |
| C(42) | 3123 | 8332 | 2686 | 74 (8) |
| C(43) | 3085 | 9427 | 3375 | 81 (8) |
| C(44) | 3535 | 9714 | 4194 | 72 (7) |
| C(45) | 2583 | 8905 | 4324 | 54 (6) |
| C(46) | 1901 | 7810 | 3635 | 54 (6) |
| N(2) | 174 (14) | 3442 (14) | 2860 (10) | 40 (4) |
| C(51) | 883 | 2828 | 2420 | 55 (6) |
| C(52) | 1213 (16) | 2020 (15) | 2696 (10) | 71 (7) |
| C(53) | 1943 | 1419 | 2276 | 101 (10) |
| C(54) | 2341 | 1626 | 1580 | 117 (11) |
| C(55) | 2010 | 2434 | 1304 | 105 (10) |
| C(56) | 1281 | 3035 | 1724 | 67 (7) |
| N(3) | −2322 (14) | 4757 (13) | 1893 (10) | 34 (4) |
| C(61) | −2614 (23) | 4619 (20) | 1084 (12) | 61 (8) |
| C(62) | −1737 | 4856 | 620 | 102 (12) |
| C(63) | −2128 | 4688 | −256 | 155 (18) |
| C(64) | −3396 | 4282 | −668 | 114 (12) |
| C(65) | −4272 | 4044 | −203 | 138 (14) |
| C(66) | −3881 | 4213 | 673 | 129 (15) |
| Cl | 8948 (6) | 1920 (6) | 4020 (4) | 75 (2) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table III.** Selected Bond Distances (Å) and Bond Angles (deg)

Bond Distances

| | | | |
|---|---|---|---|
| Pd(1)–Pd(2) | 2.694 (2) | Pd(1)–Pd(3) | 2.741 (2) |
| Pd(1)–P(1) | 2.284 (6) | Pd(1)–N(1) | 2.042 (16) |
| Pd(1)–N(3) | 2.139 (15) | Pd(2)–Pd(3) | 2.691 (2) |
| Pd(2)–P(2) | 2.271 (6) | Pd(2)–N(1) | 2.009 (15) |
| Pd(2)–N(2) | 2.071 (16) | Pd(3)–P(3) | 2.289 (6) |
| Pd(3)–N(2) | 2.052 (16) | Pd(3)–N(3) | 2.155 (15) |
| P(1)–C(11) | 1.783 (24) | P(1)–C(13) | 1.844 (32) |
| P(1)–C(15) | 1.822 (24) | C(11)–C(12) | 1.475 (33) |
| C(13)–C(14) | 1.489 (38) | C(15)–C(16) | 1.515 (34) |
| P(2)–C(21) | 1.818 (25) | P(2)–C(23) | 1.844 (23) |
| P(2)–C(25) | 1.836 (23) | C(21)–C(22) | 1.553 (34) |
| C(23)–C(24) | 1.550 (34) | C(25)–C(26) | 1.486 (32) |
| P(3)–C(31) | 1.784 (26) | P(3)–C(33) | 1.862 (30) |
| P(3)–C(35) | 1.805 (36) | C(31)–C(32) | 1.551 (39) |
| C(33)–C(34) | 1.424 (38) | C(35)–C(36) | 1.420 (46) |
| N(1)–C(46) | 1.450 (21) | N(2)–C(51) | 1.398 (23) |
| N(3)–C(61) | 1.285 (22) | | |

Bond Angles

| | | | |
|---|---|---|---|
| Pd(3)–Pd(1)–Pd(2) | 59.3 (1) | Pd(3)–Pd(2)–Pd(1) | 61.2 (1) |
| Pd(2)–Pd(3)–Pd(1) | 59.4 (1) | Pd(2)–N(1)–Pd(1) | 83.4 (6) |
| Pd(3)–N(2)–Pd(2) | 81.5 (6) | Pd(3)–N(3)–Pd(1) | 79.4 (5) |
| N(3)–Pd(1)–N(1) | 157.7 (6) | N(2)–Pd(2)–N(1) | 158.6 (6) |
| N(3)–Pd(3)–N(2) | 158.7 (6) | N(1)–Pd(1)–P(1) | 99.6 (5) |
| N(3)–Pd(1)–P(1) | 102.6 (4) | N(1)–Pd(2)–P(2) | 102.0 (5) |
| N(2)–Pd(2)–P(2) | 99.1 (5) | N(2)–Pd(3)–P(3) | 101.0 (5) |
| N(3)–Pd(3)–P(3) | 99.9 (4) | | |

"$NPh^{2-}$" fragment that rapidly reacts with metal precursor, $MCl_2(PR_3)_2$, to form a metal–imido intermediate, $(R_3P)_2M{=}NPh$. We always observed $PhN_3$ in IR spectra of the reaction mixtures. An imido species could react with $PhN_3$ to form a cyclic metal–tetrazenido complex (as observed for Ni and Pt complexes) through a 1,3-dipolar cycloaddition or could trimerize with loss of a phosphine ligand to form a trinuclear cluster in the case of palladium.

The molecular structure of the cationic complex, shown in Figure 1, contains a triangular $Pd_3$ cluster. To our knowledge, it is the first such species with bridging imido ligands. Palladium(II) dimers have been reported[7b] with bridging NHPh groups; however, only IR spectroscopic evidence was presented to support this structure. The cation of III has a pseudo-$D_{3h}$ symmetry. The $Pd_3N_3P_3$ unit is nearly coplanar, with individual displacements of the palladium, nitrogen, and phosphorus atoms from the least-squares plane not exceeding 0.112 Å. Three phenyl groups are perpendicular to the $Pd_3N_3P_3$ unit (87.2–92.7°). The protonated imido group involving N(3) exhibits disorder.

In the cation, the Pd atoms form a triangle with Pd–Pd distances of 2.694 (2), 2.691 (2), and 2.741 (2) Å and with Pd–Pd–Pd angles of 59.3 (1), 59.4 (1), and 61.2 (1)°. The Pd–Pd distances resemble those (2.579 (1)–2.93 (5) Å) found in the complexes $[Pd_3(\mu_3\text{-}CO)(\mu_2\text{-}Ph_2PCH_2PPh_2)_3][CF_3CO_2]_2$,[8] $[Pd_3(\mu_3\text{-}CO)(\mu_2\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}Cl)]^+$,[9] $[Pd_3({}^tBuCN)_5(SO_2)_2]$,[10] and $[Pd_3(PPh_2)_2(PEt_3)_3Cl][BF_4]$.[11] For comparison Pd–Pd = 2.751 Å[12] in the pure metal.

The Pd–N distances (2.009–2.155 Å) are indicative of Pd–N single bonds, since a metal–nitrogen single bond is expected to lie within 1.95–2.15 Å.[13] The Pd(1)–N(3) and Pd(3)–N(3) bond distances (2.14 (2)–2.16 (2) Å) are significantly longer than the other four Pd–N distances. This complex exhibits a strong N–H absorption at 3102 $cm^{-1}$ in its solid-state (KBr) IR spectrum. Presumably, N(3) is protonated, which induces the phenyl group disorder and elongation of Pd–N(3) and Pd(1)–Pd(3) bond distances as well.

In terms of bonding, we note that each palladium atom is in the +2 oxidation state and that, if the Pd–Pd bonds within the $Pd_3$ triangle are single two-electron bonds, each palladium atom has a 16-electron configuration. This assignment is supported by the equivalence of the Pd–P distances (2.284 (6), 2.271 (6), and 2.289 (6) Å) as well as by their similarity to the PdP distances of 2.294 (5) and 2.300 (4) Å found[14] in $Pd(N_4Ph_2)_2(PEt_3)_2$ and in the trinuclear Pd(II) cluster $Pd_3(\mu_3\text{-}S)_2(S_2C_2O_4)(PMe_3)_4$,[14] where Pd–P values lie between 2.292 (2) and 2.307 (2) Å. The total number of valence electrons in the cluster is 42, consistent with the fact that, in the platinum and palladium triangles of $[M_3(CO)_3L_3]$, $[M_3(CO)_3L_4]$ (L = $PR_3$),[15] and other complexes,[8-11] the cluster can have a total of either 42 or 44 valence electrons.

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DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer.

**Supplementary Material Available:** Tables of data collection parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (9 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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# Preparation and Study of the $Fe_2^+$–Benzyne Ion in the Gas Phase

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Previous studies have indicated that transition-metal dinuclear ions have reactivities very different from those of their constituent monoatomic ionic species.[1,2] One way to compare this is to study their reactivities with saturated hydrocarbons. For example, while $Co^+$ and $Fe^+$ are both very reactive with small alkanes, their dinuclear cluster ions $Fe_2^+$, $Co_2^+$, and $CoFe^+$ are unreactive.[3,4] Interestingly, the coordination of a seemingly very simple ligand can alter this reactivity completely. A study by Freas and Ridge indicated that $Co_2CO^+$ is reactive with small alkanes, in contrast to the inertness of the bare dinuclear species, and they explained this enhanced reactivity in terms of polarization induced by the carbonyl ligand.[4] However, more extensive study of the reactivities of dinuclear cluster ions and the effect of added ligands is necessary before the underlying factors governing the reactivity can be assessed in a systematic manner. Here we report on the preparation and the reactivity of the $Fe_2^+$–benzyne ion in the gas phase.

The study of transition-metal benzyne complexes is interesting because the transition-metal center greatly stabilizes the highly reactive benzyne ligand. Benzyne itself is very useful synthetically yet difficult to isolate and characterize because of its high degree of unsaturation.[5,6] A coordinatively unsaturated transition-metal benzyne complex is especially interesting because the metal center can potentially open up a wide variety of reaction channels by virtue of its oxidative addition ability, with the benzyne ligand then seeking whatever pathway available to satisfy its high degree of unsaturation. Our recent studies on the chemistry of $Fe^+$–benzyne with small alkanes and alkenes provide many examples of this reaction pattern, with $Fe^+$ acting as the reaction initiation center via its ability to oxidatively add into C–C and/or C–H bonds.[7,8]

All experiments in this study were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer previously described in detail.[9] The laser desorption method for generating gas-phase transition-metal ion species, the collision-induced dissociation (CID) experiment, and the pulsed-valve technique to manipulate gas-phase reagents have all been described previously in detail.[10-12]

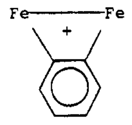
Table I. Reactions of $Fe_2C_6H_4^+$ with Alkanes

| alkane | product | rel intens, % |
|---|---|---|
| methane | no reacn | |
| ethane | $Fe_2C_6H_6^+ + C_2H_4$ | 85 |
| | $Fe_2C_8H_8^+ + H_2$ | 15 |
| propane | $Fe_2C_6H_6^+ + C_3H_6$ | 84 |
| | $Fe_2C_9H_8^+ + 2H_2$ | 6 |
| | $Fe_2C_9H_{10}^+ + H_2$ | 10 |
| *n*-butane | $Fe_2C_6H_6^+ + C_4H_8$ | 87 |
| | $Fe_2C_{10}H_{10}^+ + 2H_2$ | 13 |
| neopentane | $Fe_2C_7H_8^+ + C_4H_8$ | 100 |

The $Fe_2C_6H_4^+$ ion is prepared in the following sequence. Laser-generated $Fe^+$ first reacts with pulsed-in chlorobenzene to form $FeC_6H_4^+$,[13] which is then isolated by swept double-resonance ejections[14] and reacted with $Fe(CO)_5$ pulsed in through a second pulsed valve. The product ion $Fe_2(C_6H_4)(CO)_3^+$ is isolated and then undergoes CID at 44 eV in background argon, stripping the carbonyls away consecutively to give $Fe_2C_6H_4^+$, which is then isolated, and its reactions with other species are studied. An alternative pathway would be to first prepare $Fe_2^+$ by CID on $Fe_2(CO)_3^+$, which is in turn prepared from the reaction of $Fe^+$ with $Fe(CO)_5$. However, no $Fe_2C_6H_4^+$ is formed from the reaction of $Fe_2^+$ with chlorobenzene. Instead, it gives the condensation product $Fe_2C_6H_5Cl^+$ exclusively, which reacts further to give the secondary products $FeC_{12}H_{10}^+$, presumed to be $Fe^+$–biphenyl, and $FeCl_2$. This provides another example of the dramatic change in reactivity upon going from $Fe^+$ to $Fe_2^+$.

Unfortunately, the limited number of rf excitation pulses available on our instrument prevented further isolation and structural studies on the product ions, such as CID experiments. However, comparison of the chemistry observed here with that of $Fe^+$–benzyne could still provide some interesting insights into certain mechanistic aspects.

Previous studies on dinuclear transition-metal benzyne complexes in solution suggest a bridging benzyne ligand between the two metal centers.[15] Such a structure for $Fe_2^+$–benzyne is shown in I. CID of $Fe_2C_6H_4^+$ at 13 eV yields $FeC_6H_4^+$ exclusively. As CID energy increases, both $FeC_6H_4^+$ and $Fe^+$ are observed, with the latter accounting for ∼15% of the fragment ions at 41 eV. These results, coupled with the absence of any $Fe_2^+$ fragment, are consistent with $D^\circ(Fe^+{-}C_6H_4) \geq D^\circ(Fe^+{-}Fe)$, previously reported to be 76 ± 10[7] and 62 ± 5 kcal/mol,[16] respectively. CID at a collision energy of 13 eV of a closely related yet less symmetrical species, $CoFeC_6H_4^+$, prepared by the above sequence from the reaction of $CoC_6H_4^+$ with $Fe(CO)_5$, gives ∼65% $CoC_6H_4^+$ and ∼35% $FeC_6H_4^+$, at least consistent with the bridging structure.



I

Previous studies have shown that $FeC_6H_4^+$ reacts sequentially with chlorobenzene to form a series of polymerization product ions consisting of iron polyphenylene and uncomplexed polyphenylene ions up to hexaphenylene.[7,13,17] In contrast, $Fe_2C_6H_4^+$ reacts with chlorobenzene by cleavage of the cluster ion, yielding $FeC_{12}H_9^+$ exclusively, with no further reactions observed. One

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