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Synthesis, Characterization, and Equilibria of Palladium(II) Nitrile, Alkene, and Heterometallacyclopentane Complexes Involved in Metal Nitro Catalyzed Alkene Oxidation Reactions

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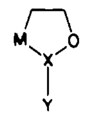
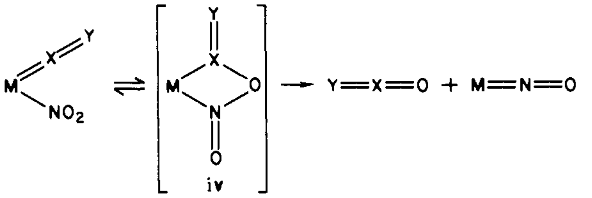
Abstract: Treatment of *trans*-$Pd(CH_3CN)_2Cl_2$ with $AgNO_2$ in acetonitrile gives *cis*-$Pd(CH_3CN)_2ClNO_2$ (**1**) that partially dissociates in chloroform solution to give $[Pd(CH_3CN)ClNO_2]_2$ (**2**). Alkenes react with **1** or **2** to give the alkene nitro complexes $[Pd(alkene)ClNO_2]_2$ (**3**), the *cis*-cyclooctene member of which has been isolated and fully characterized. Complexes **3** subsequently undergo internal cyclization by nucleophilic attack of a nitro oxygen atom on the coordinated alkene to give heterometallacyclopentane (chelated alkyl nitrite) complexes $[\overline{Pd(N(=O)OCR_2CR_2})Cl]_2$ (**4**), in which the alkyl substituents (if any) are preferentially located on the carbon β to Pd. Representative examples of these metallacycles have been isolated, and complex **4g** derived from the substituted norbornene dicyclopentadiene has been characterized by a single-crystal X-ray structure determination. $Pd_2Cl_2(C_{10}H_{12}NO_2)_2{\cdot}CH_2Cl_2$ crystallizes in the space group *Pbca* with $a = 24.717$ (6) Å, $b = 9.733$ (2) Å, $c = 20.655$ (5) Å, $V = 4969$ (1) Å^3, and $Z = 8$ at 120 K. The final discrepancy indices were $R_1(F_o) = 0.062$ and $R_2(F_o) = 0.077$. The Pd–Cl bond distances trans to carbon (2.499 (4) and 2.491 (4) Å) are longer than those trans to nitrogen (2.331 (4) and 2.328 (4) Å). The Pd–N distances (1.94 (1) and 1.95 (1) Å) are among the shortest reported to date. Complexes **1–4** are all in rapid (often NMR time scale) equilibrium with each other under the reaction conditions. (Similar behavior is observed for the previously known dichloro analogues of complexes **1–3**.) Although quantitative data regarding these equilibria are not obtainable, qualitative kinetic and thermodynamic observations are presented that are relevant to the extensive Pd(II)-mediated chemistry of alkenes. Metallacycles **4** are also involved in bridge cleavage and possibly ring-opening equilibria.

Background



i, X=O
ii, X=O; Y=H, alkyl
iii, X=N; Y=O

For over 10 years, a wide variety of metal-mediated O atom transfer reactions have been suggested to proceed via heterometallacyclic complexes, but very little concrete evidence for such intermediates has been forth coming.[1–4] For example, Mimoun and others have proposed that heterometallacyclopentanes **i** and **ii** are responsible for the oxidation of alkenes by metal dioxygen and alkyl peroxide complexes, respectively.[1] The only such species that have been observed, however, are derived from highly electron-deficient alkenes or from d^{10} transition metals.[2] Similarly, heterometallacyclobutanes **iv** have been proposed as intermediates in metal nitro mediated oxidations of CO, CS, and NO (eq 1).[3] In this case, no fully characterized model compounds have been reported.[4]


(1)

In the course of extending nitro group O atom transfer to other substrates, we have found that *cis*-bis(acetonitrile)chloronitropalladium(II) (**1**) effects the oxidation of alkenes via readily detectable alkene and type **iii** heterometallacyclopentane complexes.[5] We report here details of the synthesis and characterization of representative examples of each of these compounds, together with qualitative observations concerning the facile and multiple equilibria which link them (Scheme I).

Results

Catalyst Preparation and Characterization. Yellow *cis*-bis(acetonitrile)chloronitropalladium(II) (**1**) is readily prepared in a one pot synthesis by dissolving commercial palladium dichloride

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(1) For leading references see: (a) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734–750. (b) Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1–29. (c) Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981. (d) Di Furia, F.; Modena, G. *Pure Appl. Chem.* **1982**, *54*, 1853–1866. (e) Minoun, H.; Seree De Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37–50. (f) Arakawa, H.; Moro-Oka, Y.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2958–2961. (g) Read, G.; Walker, P. J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 883–888. (h) Read, G. *J. Mol. Catal.* **1978**, *4*, 83–84. (i) Tang, R.; Mares, F.; Neary, N.; Smith, D. E. *J. Chem. Soc., Chem. Commun.* **1979**, 274–275. (j) Purcell, K. F. *J. Organomet. Chem.* **1983**, *252*, 181–185. (k) Lyons, J. *Aspects Homogeneous Catal.* **1977**, *3*, 1–136.

(2) (a) Sheldon, R. A.; Van Doorn, J. A. *J. Organomet. Chem.* **1975**, *94*, 115–129. (b) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832–5839. (c) Halfpenny, J.; Small, R. W. H. *J. Chem. Soc., Chem. Commun.* **1979**, 879–880. (d) Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 161–166. (e) **Note Added in Proof**: A metallocyclic intermediate has recently been characterized in the reaction of $Pt(PPh_3)_2O_2$ with (*E*)-2-butenal: Broadhurst, M. J.; Brown, J. M.; John, R. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 47–48.

(3) (a) Efraty, A.; Arneri, R.; Sikora, J. *J. Organomet. Chem.* **1975**, *91*, 65–70. (b) Ileperuma, O. A.; Feltham, R. D. *J. Am. Chem. Soc.* **1976**, *98*, 6039–6040. (c) Doughty, D. T.; Gordon, G.; Stewart, J. P., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2645–2648. (d) Doughty, D. T.; Stewart, R. P., Jr.; Gordon, G. *J. Am. Chem. Soc.* **1981**, *103*, 3388–3395. (e) Kriege-Simondsen, J.; Bailey, T. D.; Feltham, R. D. *Inorg. Chem.* **1983**, *22*, 3318–3323. (f) For a comprehensive bibliography of O atom transfer reactions of metal nitro complexes see: Andrews, M. A.; Chang, T. C.-T.; Cheng, C. F. *Organometallics*, in press.

(4) Possible spectroscopic evidence for a metallacyclic intermediate in O atom transfer to CO in $[Fe(PPh_3)_2(CO)_3(NO_2)]^+$ has been reported (Baker, P. K.; Broadley, K.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1980**, 775). Notably absent, however, were any spectroscopic features attributable to the metallacyclic functionality itself, e.g., $\nu_{C=O}$ and $\nu_{N=O}$.

(5) (a) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894–2896. (b) Andrews, M. A.; Cheng, C.-W. F. *J. Am. Chem. Soc.* **1982**, *104*, 4268–4270. (c) Andrews, M. A.; Chang, T. C.-T., Cheng, C.-W. F.; Kelly, K. P. *Organometallics*, in press.

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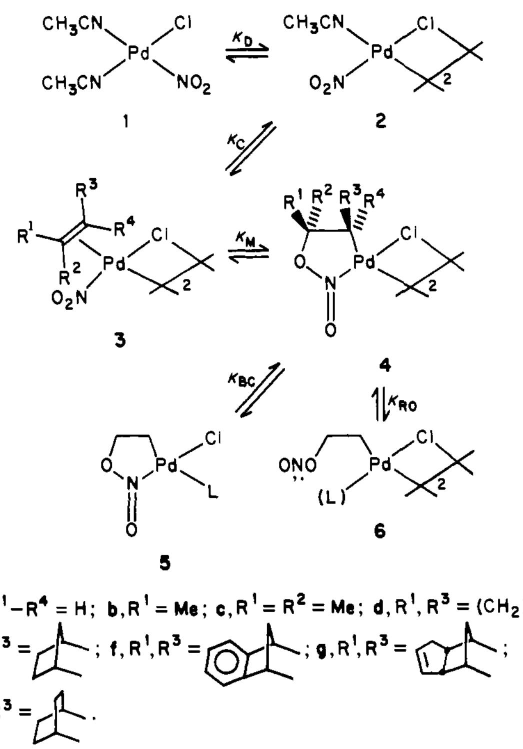
Scheme I[a]



in acetonitrile to give *trans*-bis(acetonitrile)dichloropalladium(II),[6] followed by in situ treatment with 1 equiv of silver nitrite. The nearly equal intensities of the two methyl C–H stretching modes in solid-state infrared spectra of **1** are indicative of a cis geometry for the acetonitrile ligands.[6b] This is also supported by the observation of a very slight splitting of the CN stretch in $Pd(CD_3CN)_2ClNO_2$ which is not seen in *trans*-$Pd(CD_3CN)_2Cl_2$. (In the protio species the CN stretch is mixed via Fermi resonance with a $\delta_{CH} + \nu_{CC}$ combination mode.[7] The vibrational frequencies assigned to the nitro group ((mull spectra): 1451, 1335, 826, and 600 cm^{-1}, confirmed by ^{15}N and ^{18}O labeling) clearly show that the nitro group is terminally N bonded.[8] These frequencies are only slightly shifted in CD_3CN (1460, 1338 cm^{-1}) and $CDCl_3$ (1478, 1315 cm^{-1}) solution spectra. While the former solutions are yellow as expected, the latter are orange and exhibit infrared peaks attributable to free acetonitrile, consistent with formation of dimer **2** (K_D, top of Scheme I). Similar behavior has been observed for $Pd(RCN)_2Cl_2$ complexes.[9,10] The absence of significant changes in the vibrational frequencies of the nitro group indicates that dimer formation occurs through chloride bridging, not nitro bridging.[8]

Room-temperature ^1H NMR spectra of solutions of nitro complex **1** in $CDCl_3$ (which contain monomer **1**, dimer **2**, and free acetonitrile) show only one singlet at 2.19 ppm resulting from dynamic averaging of the free and coordinated acetonitrile present. At −56 °C, the exchange rate is slow on the NMR time scale and four peaks are observed at 2.53, 2.48, 2.43, and 2.12 ppm, the first three due to coordinated nitrile and the latter to free nitrile. (The nitrile chemical shifts are significantly temperature dependent, free acetonitrile having a chemical shift of 2.00 ppm at room temperature.) The equal intensity peaks at 2.53 and 2.43 ppm are tentatively assigned to the two types of methyl groups in monomer **1** while the larger peak at 2.48 ppm is assigned to the methyl groups in dimer **2**.[11] The monomer–dimer equilibrium constant K_D is clearly temperature dependent favoring the monomer at lower temperatures. The mixed chloro nitro complexes **1** and **2** appear to be relatively stable toward disproportionation since only a small peak due to the dichloro complexes is seen in ^1H NMR spectra of solutions of **1**.

Alkene Nitro Complexes 3. The palladium alkene complexes $[Pd(alkene)Cl_2]_2$, though of limited stability, are readily prepared from bis(benzonitrile)palladium dichloride.[12] The reactions of nitro complex **1** with alkenes are analogous, except for the added complication of subsequent facile metallacycle formation (vide infra). Addition of most alkenes to $CDCl_3$ solutions of **1** leads to partial displacement of acetonitrile by alkene as evidenced by an instantaneous color change from orange to yellow and the appearance of a second C═C stretching frequency in the infrared at ~100 cm^{-1} below that of the free alkene. In the ^1H NMR, the dynamically averaged acetonitrile methyl resonance shifts upfield due to the higher fraction of free acetonitrile now present. The alkene vinyl and allyl resonances shift downfield with free and coordinated alkene also exchanging on the NMR time scale.[13] This exchange is difficult to freeze out for most alkenes, even at −80 °C.

The only alkene nitro complex that we have been able to isolate from these solutions and fully characterize is dimer **3d** derived from *cis*-cyclooctene. Most other alkenes investigated bind less strongly to Pd(II), are more rapidly oxidized via metallacycles **4**, or both. Aside from its unusual stability (no decomposition in dry air for over 2 weeks at room temperature), alkene nitro complex **3d** appears to be quite typical. The C═C stretch is observed ($CDCl_3$ solution) at 1525 cm^{-1} (vs. 1653 cm^{-1} for free *cis*-cyclooctene and 1514 cm^{-1} for the analogous dichloro complex). The nitro group vibrations are observed at 1469, 1312, and 819 cm^{-1}. In the ^1H NMR, the vinyl protons in **3d** appear as a quintet centered at 6.16 ppm (vs. 5.62 ppm for free *cis*-cyclooctene and 6.20 ppm for the dichloro analogue), while the allylic protons resonate at 2.31 ppm (vs. 2.12 and 2.31 ppm for free alkene and dichloro analogue, respectively).

Heterometallacycles 4. Alkene nitro complexes **3** undergo internal cyclization to give equilibrium concentrations of heterometallacyclopentanes **4** (middle of Scheme I) in a period of seconds (isobutylene[14] and norbornene) to minutes (ethylene and propylene). Although these species are usually readily detectable by spectroscopic means, isolation and unambiguous characterization were only possible in the case of bicyclic alkenes. Internal and cyclic alkenes have very low metallacycle formation constants

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[6] (a) Walton, R. A. *Spectrochim. Acta* **1965**, *21*, 1795–1801. (b) Walton, R. A. *Can. J. Chem.* **1968**, *46*, 2347–2352. (c) Wayland, B. B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971–976. (d) Hegedus, L. S.; Williams, R. E.; McGuire, M. A.; Hayashi, T. *J. Am. Chem. Soc.* **1980**, *102*, 4973–4979.

[7] We believe that the literature assignments[6a] for the ν_{CN} and the $\delta_{CH} + \nu_{CC}$ combination mode in $Pd(CH_3CN)_2Cl_2$ should be reversed. We attribute the reversal to an incorrect assignment of the ν_{CC} mode which we assign to a sharp weak peak at 955 cm^{-1} (shifting to 867 cm^{-1} on deuteration) rather than 970 cm^{-1} as given in the literature.

[8] Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55–132.

[9] Kitching, W.; Moore, C. J.; Doddrell, D. *Inorg. Chem.* **1970**, *9*, 541–549.

[10] For $Pd(RCN)_2Cl_2$ (R = Me, $PhCH_2$) complexes, ^1H NMR spectra in $CDCl_3$ show that partial nitrile dissociation occurs but, in contrast to $Pd(MeCN)_2ClNO_2$, free and coordinated nitrile do not exchange on the NMR time scale at room temperature. Over a period of ~3 h, some $PdCl_2$ is observed to precipitate until a steady-state equilibrium is achieved. By integrating free vs. coordinated nitrile for the more soluble phenylacetonitrile complexes and weighing the $PdCl_2$ formed in four samples with different $[Pd(II)]_o$ and $[RCN]_o$, approximate dissociation constants at 27 °C were obtained: $K_{D^1} = [(PdLCl_2)_2][L]^2/[PdL_2Cl_2]^2 = 0.10 \pm 0.05$ M, $K_{D^2} = [L]^2/[(PdLCl_2)_2] = 0.8 \pm 0.3$ M. The large errors are due to the magnified effect that small experimental errors have when taking small differences between large numbers. Qualitatively, the following order of ligating strength is observed for weak ligands toward $PdCl_2$: $HCONMe_2 \ll PhCH_2CN \approx PhCN < MeCN \ll Me_2SO$.

[11] The dimer can theoretically have either a C_{2h} (trans) or C_{2v} (cis) geometry. We would expect the methyl groups in both isomers to resonate at very nearly the same frequency.

[12] (a) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882–884. (b) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. *Compr. Organomet. Chem.* **1982**, *6*, 351–362.

[13] Exchange of free and coordinated alkene on the NMR time scale has been observed in other Pd(II) alkene complexes: (a) Partenheimer, W.; Durham, B. *J. Am. Chem. Soc.* **1974**, *96*, 3800–3805. (b) Ban, E.; Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1974**, *69*, 455–472.

[14] The equilibration of the isobutylene alkene and heterometallacyclopentane complexes **3c** and **4c** does not occur on the NMR time scale, however, even at 60 °C.

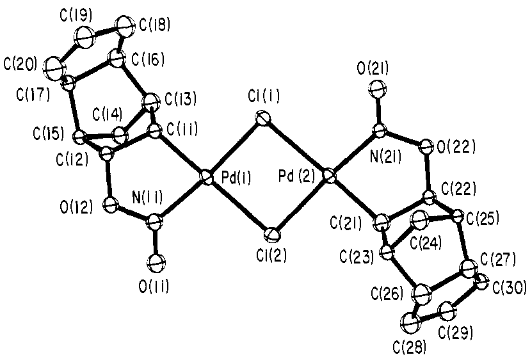
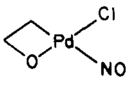


Figure 1. Molecular structure of the palladium metallacycle **4g**. Thermal ellipsoids drawn at the 50% probability level.

(K_M), while simple terminal alkenes have K_M values of roughly 1 and decompose to oxidized products[5] at about 30%/h at room temperature.

The complex **4e** derived from norbornene has been characterized by IR, ^1H and ^{13}C NMR, elemental analysis, osmometry molecular weight, and, for a derivative, by X-ray crystallography. The most distinctive spectral feature of all these metallacyclic species is a strong N=O stretch near 1615 cm^{-1} that has been confirmed by ^{15}N and ^{18}O labeling studies. This can be compared with values of 1550 and 1500 cm^{-1} observed for simple alkyl nitrite complexes of Ir(II) and Ru(II), respectively.[15] The lower frequencies in the case of the Ir and Ru complexes vs. the Pd metallacycles may be due to a difference in geometry. Free alkyl nitrites exhibit two N=O stretches at 1680–1650 and 1625–1610 cm^{-1} assigned to trans and cis isomers, respectively, about the ON—OR bond.[16] In the case of chelated alkyl nitrite metallacycles **4** the O=N and O—R groups are constrained to be trans but are almost certainly cis for steric reasons in the case of the Ir and Ru complexes. The N–O and C–O stretches and the ONO bending modes have also been assigned (see Experimental Section), but these assignments are somewhat idealized since the distribution of isotopic shifts observed indicates that substantial mode mixing occurs.

^1H NMR spectra show that the protons on the carbon bearing the nitrite group resonate at about 4.0–4.5 ppm, similar to that of free alkyl nitrites and the Ru(II) alkyl nitrite complexes. The protons on the carbon bound to palladium resonate at 2.0–4.5 ppm depending on the number of alkyl substituents present on both the metallacyclic carbon atoms. From these assignments and from the observed decomposition pathways,[5] it is evident that the alkyl substituent(s) are preferentially located on the β-carbon of the metallacycle. In the metallacycles derived from bicyclic alkenes, the two metallacyclic methine protons resonate at almost the same frequency leading to a second-order AB quartet at ~4.3 ppm. The carbon atom bonded to the nitrite group in metallacycle **4e** has a ^{13}C NMR chemical shift of 69.5 ppm, comparable to 68.2 ppm for the corresponding carbon in *n*-butyl nitrite. The carbon bound to palladium resonates at 94.9 ppm. An osmometry molecular weight determination confirmed that the norbornene metallacycle is dimeric in solution, ruling out an alternative structural type **v** which is difficult to distinguish unambiguously from metallacycles **4** by spectroscopic means.



v

Molecular Structure of $[Pd_2Cl_2(C_{10}H_{12}NO_2)_2]\cdot CH_2Cl_2$ (4g). Conclusive evidence for the structure of metallacycles **4** is provided by a single-crystal X-ray structure determination of metallacycle **4g** derived from the substituted norbornene dicyclopentadiene. An ORTEP drawing of the molecule is shown in Figure 1, and selected bond distances and angles are listed in Tables I and II. Although not required to be so crystallographically, the metallacycle is nearly centrosymmetric. The cyclopentene groups (C(16)–C(20) and C(26)–C(30)) are endo to the norbornane skeletons (C(11)–C(17) and C(21)–C(27)), while the metallacyclic groups are exo. The solvent molecule is present at full occupancy but with a large degree of thermal motion.

Table I. Selected Bond Distances (Å) for $[Pd_2Cl_2(C_{10}H_{12}NO_2)_2]\cdot CH_2Cl_2$[a]

Pd(1)–Cl(1)	2.331 (4)	Pd(2)–Cl(1)	2.491 (4)
Pd(1)–Cl(2)	2.499 (4)	Pd(2)–Cl(2)	2.328 (4)
Pd(1)–N(11)	1.94 (1)	Pd(2)–N(21)	1.95 (1)
Pd(1)–C(11)	1.98 (2)	Pd(2)–C(21)	1.99 (2)
N(11)–O(11)	1.19 (2)	N(21)–O(21)	1.18 (2)
N(11)–O(12)	1.36 (2)	N(21)–O(22)	1.40 (2)
C(11)–C(12)	1.53 (2)	C(21)–C(22)	1.52 (2)
C(12)–O(12)	1.48 (2)	C(22)–O(22)	1.46 (2)
C(18)–C(19)	1.48 (3)	C(28)–C(29)	1.46 (3)
C(19)–C(20)	1.34 (3)	C(29)–C(30)	1.38 (2)

[a] Estimated standard deviations in the least-significant figure(s) are enclosed in parentheses in this and subsequent tables.

Table II. Selected Bond Angles (deg) for $[Pd_2Cl_2(C_{10}H_{12}NO_2)_2]\cdot CH_2Cl_2$

Pd(1)–Cl(1)–Pd(2)	92.6 (1)	Pd(1)–Cl(2)–Pd(2)	92.5 (1)
Cl(1)–Pd(1)–N(11)	174.0 (4)	Cl(2)–Pd(2)–N(21)	175.2 (4)
Cl(2)–Pd(1)–C(11)	178.6 (5)	Cl(1)–Pd(2)–C(21)	179.3 (5)
Cl(1)–Pd(1)–Cl(2)	87.3 (1)	Cl(1)–Pd(2)–Cl(2)	87.6 (1)
Cl(1)–Pd(1)–C(11)	91.3 (5)	Cl(2)–Pd(2)–C(21)	92.2 (5)
Cl(2)–Pd(1)–N(11)	97.8 (4)	Cl(1)–Pd(2)–N(21)	96.2 (4)
N(11)–Pd(1)–C(11)	83.6 (6)	N(21)–Pd(2)–C(21)	84.0 (6)
O(11)–N(11)–Pd(1)	129 (1)	O(21)–N(21)–Pd(2)	129 (1)
O(11)–N(11)–O(12)	113 (1)	O(21)–N(21)–O(22)	113 (1)
O(12)–N(11)–Pd(1)	118 (1)	O(22)–N(21)–Pd(2)	118 (1)
N(11)–O(12)–C(12)	114 (1)	N(21)–O(22)–C(22)	112 (1)
Pd(1)–C(11)–C(12)	111 (1)	Pd(2)–C(21)–C(22)	110 (1)
O(12)–C(12)–C(11)	112 (1)	O(22)–C(22)–C(21)	115 (1)
C(16)–C(18)–C(19)	103 (2)	C(26)–C(28)–C(29)	106 (2)
C(18)–C(19)–C(20)	114 (2)	C(28)–C(29)–C(30)	113 (2)
C(17)–C(20)–C(19)	111 (2)	C(27)–C(30)–C(29)	109 (2)

The coordination geometry about the palladium atoms is nearly square planar, as expected for Pd(II). The four cis interligand angles about each Pd are all within 8° of right angles and sum to 360°, and the maximum deviation of any of the ligating atoms from either of the five-atom $PdCl_2CN$ coordination planes is 0.099 (13) Å for N(11).

The Pd–Cl bond distances trans to carbon atoms (Pd(1)–Cl(2) and Pd(2)–Cl(1)) are about 0.17 Å longer than those trans to nitrogen atoms. Studies of this trans influence in similar compounds,[17] including palladium metallacyclic complexes,[18] show that Pd–Cl distances trans to C (2.446–2.527 Å) are always significantly longer than Pd–Cl distances trans to N or P (2.331–2.429 Å). In the present case the Pd–Cl distances trans to C (2.499 (4) and 2.491 (4) Å for Pd(1) and Pd(2), respectively) are normal, as are the Pd–C(sp^3) distances[18,19] (1.98 (2) and 1.99 (2) Å for Pd(1)–C(11) and Pd(2)–C(21), respectively). In contrast, the Pd–Cl distances trans to N (2.331 (4) and 2.328 (4)

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[15] (a) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1243–1246. (b) Walsh, J. L.; Bullock, R. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 865–869.

[16] (a) Tarte, P. *J. Chem. Phys.* **1952**, *20*, 1570–1575. (b) Klaboe, P.; Jones, D.; Lippincott, E. R. *Spectrochim. Acta, Part A* **1967**, *23A*, 2957–2971.

[17] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

[18] (a) Drew, M. G. B.; Riedl, M. J.; Rodgers, J. *J. Chem. Soc., Dalton Trans.* **1972**, 234–237. (b) Hegedus, L. S.; Anderson, O. P.; Zetterberg, K.; Allen, G.; Siirala-Hansen, K.; Olsen, D. J.; Packard, A. B. *Inorg. Chem.* **1977**, *16*, 1887–1894. (c) Alyea, E. C.; Dias, S. A.; Ferguson, G.; McAlees, A. J.; McCrindle, R.; Roberts, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 4985–4989. (d) Goel, A. B.; Goel, S.; Vanderveer, D. *Inorg. Chim. Acta* **1981**, *54*, L267–L269. (e) Oliver, J. D.; Mullica, D. F.; Milligan, W. O. *Inorg. Chem.* **1982**, *21*, 3284–3286. (f) Youngs, W. J.; Mahood, J.; Simms, B. L.; Swepston, P. N.; Ibers, J. A.; Maoyu, S.; Jinling, H.; Jiaxi, L. *Organometallics* **1983**, *2*, 917–921.

[19] Bennett, M. A.; Johnson, R. N.; Robertson, G. B.; Tomkins, I. B.; Whimp, P. O. *J. Am. Chem. Soc.* **1976**, *98*, 3514–3523.

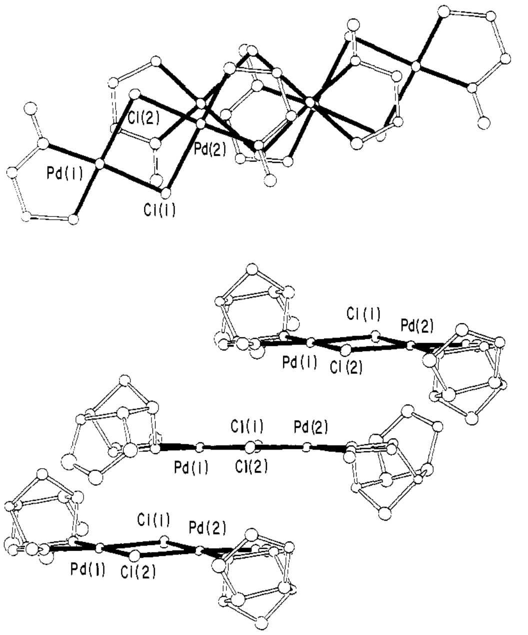

Figure 2. Columnar stacking of the palladium metallacycles. (Thermal ellipsoids drawn at the 30% probability level.) Top: view along the normal to the plane of the Pd_2Cl_2 core with substituted norbornene ligands removed for clarity. Bottom: view perpendicular to that above. Interplanar spacing is approximately 3.5 Å.

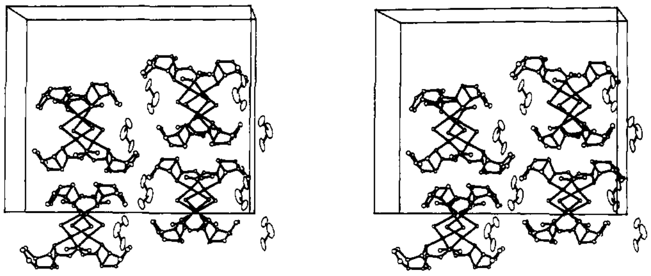

Figure 3. Stereoview of the unit cell packing in the crystal structure of **4g**. The view is along the crystallographic *b* axis with the origin at the lower right, back corner.

Å, respectively) are at the short end of the normal range, as are the Pd–N distances which at 1.94 (1) and 1.95 (1) Å are among the shortest reported to date.[18a–c,20] Significantly shorter Pd–N bond distances are found in $Pd_4(\mu\text{-}NO)_2(\mu\text{-}O_2CCH_3)_6$ for which the average Pd–N length is 1.89 (2) Å.[21] The Pd–N bond distances in the present structure are more comparable to those in palladium oxime complexes (typically 1.95–1.97 Å) which also contain an sp^2 N atom ($Pd{-}N(OH){=}CR_2$).[22] The short Pd–N bond found here for the chelated alkyl nitrite ligand is somewhat surprising in view of the very poor ligating ability found for simple alkyl nitrites toward Pd(II) (vide infra). We are not aware of any other alkyl nitrite complexes that have been characterized crystallographically; it thus remains to be seen whether short metal–nitrogen bonds are a characteristic feature of alkyl nitrite complexes.

The alkyl nitrite ligand is also involved in the most significant angular distortions from the predicted idealized geometry found in the present structure. The ligating nitrogen atoms are bent away from the cis bridging chloride ligands with N–Pd–Cl angles of 97.8 (4)° and 96.2 (4)° about Pd(1) and Pd(2), respectively, compressing the metallacyclic N–Pd–C angles to 83.6 (6) and 84.0 (6)°, respectively. Also, the exocyclic Pd—N═O angles (both 129 (1)°) are wider and the O–N–O angles correspondingly smaller (both 113 (1)°) than the idealized 120° angles expected about sp^2-hybridized nitrogen atoms. These angular distortions are essentially within a plane, however, with the sum of the angles about each nitrogen being 360°.

The metallacyclopentane rings do not appear to be strained and are not greatly puckered. Indeed the whole metallacyclic core $[Pd_2Cl_2(C_2NO)_2]$ is relatively planar, the maximum deviation from this plane being 0.128 (15) Å for C(12). The endocyclic torsion angles about the bonds Pd(1)–C(11), C(11)–C(12), C(12)–O(12), O(12)–N(11)–, and N(11)–Pd(1) are +7.4, −7.6, +3.0, +3.4, and −6.4°, respectively. The metallacycle ring involving Pd(2) is slightly more puckered, the corresponding torsion angles being −9.9, +13.6, −9.9, +1.3, and +5.3°. The greater twist present in ring 2 is also apparent when comparing the exocyclic torsion angles C(13)–C(11)–C(12)–C(15) and C(23)–C(21)–C(22)–C(25), which are 0.9 and 2.8°, respectively.

The geometries of the organic nonbornane substituents are typical.[23] The carbon–carbon double bonds in the cyclopentene fragments appear to be preferentially located in the positions farthest from the palladium atoms (C(19)–C(20) and C(29)–C(30)).

The crystal packing, shown in Figures 2 and 3, is characterized by a two-dimensional array of weakly interacting columns of metallacycles parallel to the *bc* diagonals. The columns are composed of molecules that stack along the direction perpendicular to their planar central regions and are separated in the unit cell by channels of paired dichloromethane molecules. Interactions between complexes are weak and take place primarily through contacts between metallacyclic planes within a stack. The interacting regions are slipped along the long in-plane molecular axis, with the five-atom PdC_2NO, and four-atom Pd_2Cl_2 rings positioned above each other (Figure 2a). The intermolecular contacts within these columns are all greater than or equal to the corresponding van der Waal radii sums[24] (e.g., Pd(1)···Pd(2; $^1/_2 + x, -^1/_2 - y, -z$) = 3.402 (3) Å, Cl(2)···N(21; $^1/_2 + x, -^1/_2 - y, -z$) = 3.36 (1) Å, and Cl(1)···O(11; $^1/_2 + x, ^1/_2 - y, -z$) = 3.37 (1) Å). Regions of weak solvent–complex and solvent–solvent interactions comprise the crystal packing between columns of metallacycles. The methylene chloride molecules are located at approximately $x = 0$ and $x = ^1/_2$ and are paired throughout the unit cell about inversion centers. The shortest intersolvent contact is Cl(3)···Cl(3)′ at 3.61 Å.

Discussion

Nitrile Complexes. The complexes reported here are linked by facile and multiple equilibria partially outlined in Scheme I. Nitriles are relatively weak ligands toward Pd(II), and hence both nitro complex **1** and its dichloro analogue undergo nitrile dissociation. The first dissociation constant K_D (top of Scheme I) appears to be moderately high for both complexes, while the second dissociation constant corresponding to complete loss of nitrile is only significant for the dichloro complex.[10]

Alkene Complexes. Pd(II) alkene complexes occupy a central role in a wide variety of organic synthetic applications.[25] Despite this importance, the *cis*-cyclooctene nitro complex **3d** reported here is one of the relatively few simple Pd(II) alkene complexes that have been isolated and characterized.[12,13,25,26] Quantitative

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(20) (a) Iball, J.; MacDougall, M.; Scrimgeour, S. *Acta Crystallogr., Sect. B* **1975**, *31B*, 1672–1674. (b) Clark, G. R.; Palenik, G. J. *Inorg. Chem.* **1970**, *9*, 2754–2760. (c) Fallon, G. D.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1974**, 1632–1635. (d) "Bond Index to the Determinations of Inorganic Crystal Structures (BIDICS)"; Institute for Materials Research, McMaster University: Hamilton, Ontario, Canada, 1969–1981.

(21) Podberezskaya, N. V.; Bakakin, V. V.; Kuznetsova, N. I.; Danilyuk, A. F.; Likholobov, V. A. *Dokl. Akad. Nauk SSSR* **1981**, *256*, 870–874.

(22) (a) Sheung, Ma, M.; Angelici, R. J.; Powell, D.; Jacobson, R. A. *Inorg. Chem.* **1980**, *19*, 3121–3128. (b) Hussain, M. S.; Schlemper, E. O. *Inorg. Chem.* **1979**, *18*, 1116–1121. (c) Endre, H. *Acta Crystallogr., Sect. B* **1980**, *36B*, 1347–1350.

(23) Doms, L.; Van den Enden, L.; Geise, H. J.; Van Alsenoy, C. *J. Am. Chem. Soc.*, **1983**, *105*, 158–162.

(24) van der Waals radii (Å) for Pd (1.6)[24b], Cl (1.8)[24a], O (1.4)[24a], N (1.5)[24a], and C (1.7)[24b] were taken from: (a) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

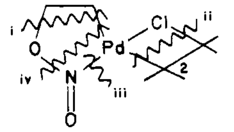
(25) Maitlis, P. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vols. 1 and 2.

data for the binding strengths of alkenes to Pd(II) are also scarce.[12b,13,26b,c,27] We had therefore originally hoped to determine the alkene complexation constants K_c for both the present system (Scheme I) and for the corresponding dichloro series, taking advantage of the acetonitrile methyl group (or the benzylic protons in the more soluble phenylacetonitrile complexes) as a convenient NMR probe. This advantage was not sufficiently large, however, to significantly improve upon the previous literature results which employed changes in alkene solubility,[27a] precipitation followed by decomposition and GC analysis,[26b] or calorimetry.[13a] The primary difficulty encountered by both us and previous workers[26b] is the presence of too many rapid equilibria.[28]

Sufficiently large qualitative differences were seen in a number of cases to be worth summarizing here. When $Pd(CH_3CN)_2Cl_2$ is treated with 1 equivalent of ethylene, cyclooctene, or an electron-rich vinyl ether, over 80% of the alkene becomes corrdinated. As might be expected, the derived complexes have therefore been isolated and characterized previously.[12a,13a,26d] The downfield shift of the vinyl protons on coordination is consistent with the primary bonding interaction being a σ donation from the filled alkene π orbital to an empty, electrophilic Pd(II) orbital. In contrast, sterically hindered bicyclic alkenes and electron-deficient acrylate esters are less than 5% coordinated under the same conditions. An exception is the difunctional alkene maleic anhydride that does coordinate. In this case the vinyl protons shift upfield on coordination rather than downfield, suggesting that the primary Pd(II)–alkene interaction is now π-back-bonding from filled Pd orbitals to the alkene π-antibonding orbitals. The alkene complexation constants for other alkenes are determined by a subtle balance of steric and electronic factors but are generally not too far removed from unity; hence, a moderate percentage of the alkene present is coordinated under normal reaction conditions. The binding of the alkenes to nitro complex **1** appears to be just slightly weaker than in the corresponding dichloro complex.

Heterometallacycles 4. Complexes **4** are the first metallacyclic species to be clearly observed either in nitro group O atom transfer reactions or in alkene oxidation reactions. As noted in the Background related species have been widely postulated[1,3,4] but have never been observed except in special cases such as with highly electron-deficient alkenes or with d^{10} metals.[2] Metallacycles **4** also contain one of the few examples of a coordinated alkyl nitrite ligand[15] and the first to be characterized crystallographically.

The chemistry of metallacycles **4** is dominated by bond making–bond breaking reactions that occur in four different places in the molecule (i–iv). Sites i, ii, and iii correspond to the metallacycle formation, bridge cleavage, and ring opening equilibria K_M, K_{BC}, and K_{RO}, respectively (Scheme I), while site iv corresponds to the formation of oxidized products.



It is somewhat surprising that metallacycle formation is readily reversible (K_M) since the cycloreversion reaction involves the breaking of a carbon–oxygen bond (i) in preference to a nitrogen–oxygen bond (iv). (The latter does occur more slowly (hours vs. minutes to seconds) resulting in the irreversible formation of oxidized products.[5]) This equilibrium does have precendent in the observations that nitro group O atom transfer to CO[3c–e] and amination of palladium(II) alkene complexes[29] may also be reversible. Quantitative values for the cyclization constants K_M are not obtainable due to the multiple equilibria present but again significant qualitative trends are readily apparent.

For terminal alkenes K_M is near unity. Thus for ethylene, propylene, and similar alkenes, metallacycles **4** account for roughly 10–30% of the palladium present on reaction of nitro complex **1** with the alkene. For 1,1-disubstituted alkenes such as isobutylene, K_M is slightly larger, with about 40–60% of the palladium being present in the form of metallacycle. In both cases the alkyl substituents appear to be located exclusively on the carbon atom β to the palladium. This would be the expected kinetic result for nucleophilic attack of the nitro oxygen atom on the coordinated alkene in **3**[30] but may also be the thermodynamically favored distribution since the cyclization is readily reversible.

For internal and cyclic alkenes, where both α- and β-substitution are present, no metallacyclic species can be detected by ^1H NMR. This follows (assuming additivity of substituent effects) from the near unity K_M values found for terminal alkenes and the fact that β-substitution is preferred over α-substitution by at least 2–3 kcal/mol. The quantitative metallacycle formation observed with norbornene, despite the α,β-disubstitution present, was initially attributed to the relief of ring strain that would accompany metallacycle formation. Although this is clearly a contributing factor, it cannot be the only one since highly strained *trans*-cyclooctene does not form a metallacycle while relatively unstrained bicyclo[2.2.2]oct-2-ene does (though to a lesser degree than norbornene). A further factor would appear to be the stability of the alkene complex. The bicyclic alkenes are sterically hinder with respect to alkene complexation, thereby shifting the equilibrium toward the metallacycle side. Conversely, *trans*-cyclooctene can readily form an alkene complex and in so doing relieve ring strain by the concomitant bending back of the alkene substitutent groups.[31] This is apparently enough to tip the closely balanced equilibrium back toward the alkene complex. We have no obvious explanation for the observation that bicyclo[3.2.1]oct-2-ene forms neither an alkene complex nor a metallacycle but nevertheless is oxidized by nitro complex **1** to the epoxide at roughly the same rate as norbornene.[5]

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(26) (a) Ketley, A. D.; Fisher, L. P.; Berlin, A. J.; Morgan, C. R.; Gorman, E. H.; Steadman, T. R. *Inorg. Chem.* **1967**, *6*, 657–663. (b) Pregaglia, G. F.; Conti, F.; Minasso, B.; Ugo, R. *J. Organomet. Chem.* **1973**, *47*, 165–178. (c) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996–7003. (d) Wakatsuki, Y.; Nozakura, S.; Murahashi, S. *Bull. Chem. Soc Jpn.* **1972**, *45*, 3426–3429. (e) A number of chelated dialkene complexes of Pd(II) are known.[12b,25]

(27) (a) Henry, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 1595–1597. (b) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163–190.

(28) In the reaction of both $Pd(RCN)_2Cl_2$ and $Pd(RCN)_2ClNO_2$ with alkenes, the NMR time scale exchange of free and coordinated alkene precludes a near ambient-temperature determination of the alkene binding constant K_C by integration of free vs. coordinated alkene. Similarly, since most of the alkene complexes cannot be isolated, the chemical shift of bound alkene can not be determined. This precludes a determination of K_C by comparison of the averaged alkene chemical shift in the in situ reaction mixture with the free and coordinated alkene chemical shifts. A crude measure of K_C is provided by the nitrile ligands that are displaced by the alkene on coordination. In the dichloro complexes, the ratio of coordinated and free nitrile (which do not exchange on the NMR time scale in either $Pd(RCN)_2Cl_2$ or $[Pd(RCN)Cl_2]_2$) is inversely related to K_C. This ratio is rather easily determined, especially for the more soluble phenylacetonitrile complexes which also have the advantage that the chemical shift of the benzylic hydrogens is clear of the alkene allylic protons. Quantitative analysis to extract K_C, however, requires an accurate knowledge of the two nitrile dissociation constants in the absence of alkene,[10] and the assumption that the only alkene complex present is $[Pd(alkene)Cl_2]_2$. The literature would suggest that this latter assumption is rather idealized.[26a,b] Our spectra, in fact, provide evidence for the presence of the mixed monomer $Pd(CH_3CN)(C_2H_4)Cl_2$. The "free" acetonitrile peak observed in the reaction of $Pd(CH_3CN)_2Cl_2$ with ethylene appears slightly downfield (2.02–2.06 ppm) of authentic free acetonitrile (2.00 ppm). This cannot be due to NMR time scale exchange with the coordinated nitrile in $Pd(CH_3CN)_2Cl_2$ or $[Pd(CH_3CN)Cl_2]_2$ since the nitrile peak due to these species is still present (~2.38 ppm). This implies that another species such as $Pd(CH_3CN)C_2H_4)Cl_2$ is present which contains a labile nitrile group exchangeable with the free acetonitrile. In the chloronitro series, a crude estimate of K_C is even easier to obtain since free and coordinated nitrile exchange on the NMR time scale in all species present. The position of the large averaged acetonitrile singlet in the in situ reaction mixture vs. the free (2.00 ppm) and coordinated (~2.38 ppm) values is proportional to K_C, again subject to the problems mentioned above for the dichloro series and the further complication of conversion to metallacycles **4** and **5**.

(29) Åkermark, B.; Bäckvall, J. E.; Hegedus, L. S.; Zetterberg, K.; Siirala-Hansen, K.; Sjoberg, K. *J. Organomet. Chem.* **1974**, *72*, 127–138.

(30) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320. (b) Chang, T. C.-T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361–7362. (c) Wright, L. L.; Wing, R. M.; Rettig, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 610–612. (d) Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335–342 and references therein.

(31) See, for example: Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653–2657.

The equilibrium K_{BC} corresponding to metallacycle bridge cleavage at site ii can be observed in the presence of certain donor ligands. Strong donor ligands such as phosphines and amines simply convert metallacycles **4** back to free alkene and ligand-substituted derivatives of **1** in time of mixing by reversing equilibria K_M, K_C, and K_D. If only 1 equiv of L/Pd is used, 50% of the metallacycle remains unreacted while the other 50% is completely converted back to free alkene and PdL_2ClNO_2. When weak donor ligands are employed, however, bridge cleavage competes with cycloreversion. Thus reaction of norbornene metallacycle **4e** with increasing amounts of acetonitrile leads to partial formation of norbornene but also in the ^{1}H NMR to a smooth and gradual lessening of the second-order character (increasing chemical shift difference) of the AB quartet associated with the metallacyclic protons. This reaction must be a simple bridge cleavage process rather than a ring opening reaction at site iii (K_{RO}), since there is only a slight change in the frequency assigned to the N=O stretch. The presence of only one set of resonances attributable to the metallacycle shows that the bridge cleavage equilibrium is rapid on the NMR time scale at room temperature.

Similar behavior is observed with the metallacycles derived from propylene and isobutylene. Variable-temperature NMR spectra of the isobutylene system show that bridge cleavage can be frozen out. At −85 °C, resonances can be observed for free alkene (4.68 and 1.74 ppm), coordinated alkene (5.13 and 1.96 ppm), free nitrile (2.12 ppm), coordinated nitrile (~2.43 ppm for **1** and **2**), metallacycle dimer **4c** (3.34 and ~1.68 ppm), and bridge-cleaved metallacycle **5c** (L = CH_3CN, 3.22, 2.30 (CH_3CN), and ~1.68 ppm). Similar reactions may partially explain the unusual spectra observed (see Experimental Section) in the reaction of ethylene with nitro complex **1**.

It has not been possible to obtain definitive evidence for the remaining proposed equilibrium, metallacyclic ring opening (K_{RO}). The low equilibrium constant for ring opening is attributed to the chelate effect present in the metallacyclic alkyl nitrite complexes. We nevertheless believe that ring opening must be occurring on the basis of the kinetic lability of Pd(II) and the poor donor character of alkyl nitrites toward Pd(II) (witness the inability of *n*-butyl nitrite to displace even the weak acetonitrile ligands in the $Pd(CH_3CN)_2Cl_2$. The importance of heterometallacycles **4** and the potentially critical role that their ring-opeing reactions may have in determining the oxidized product distributions that result from their decomposition are presented elsewhere.[5b,c]

Experimental Section

General Information. Infrared spectra were recorded on a Nicolet MX-1 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer equipped with a dual 80-MHz proton and 20-MHz carbon probe using Me_4Si as internal standard. Analyses were performed by Schwartzkopf Microanalytical Laboratories (C, H, N, M_r) or by Eleanor Norton (Cl, Pd) of this department.

Solvents were dried over molecular sieves; reagents were used as received. Reactions were usually run under nitrogen by using Schlenk techniques, although experience indicates that this should not be necessary for most of the preparations reported here.

***trans*-Bis(acetonitrile)dichloropalladium(II).**[6] Finely powdered palladium dichloride (2.00 g, 11.3 mmol) was stirred in acetonitrile (40 mL) at room temperature. The palladium dichloride partially dissolved to give a yellow solution containing suspended yellow solid. It was necessary to periodically break up chunks of unreacted starting material that formed to obtain complete conversion, a process which typically took several days. Refluxing the mixture did not seem to help in this regard. The solvent was then evaporated under vacuum to yield the desired complex (2.82 g, 96%): IR (Nujol/Fluorolube mulls) 3290 (w, $\nu_{CN} + \nu_{CC}$), 2985 (m, $\nu_{CH}(E)$), 2924 (s, $\nu_{CH}(A_1)$), 2335 (s, ν_{CN}), 2304 (m, $\delta_{CH} + \nu_{CC}$), 1412 and 1353 (m, δ_{CH}), 1022 (m, ρ_{CH}), 955 (w, ν_{CC}), 447 and 410 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.38 (s), 2.00 (s, free CH_3CN).

$Pd(CD_3CN)_2Cl_2$ was prepared by dissolving the corresponding protio complex in CD_3CN followed by evaporation of solvent after 1 day: IR (Nujol/Fluorolube mulls) 2240 (w, $\nu_{CD}(E)$), 2102 (m, $\nu_{CD}(A_1)$), 2330 (s, ν_{CN}), ~1040 (m, δ_{CD}), 836 (m, ρ_{CD}), 867 (w, ν_{CC}), 430 (w) cm^{-1}.

***cis*-Bis(acetonitrile)chloronitropalladium(II) (1).** A suspension of $Pd(CH_3CN)_2Cl_2$ was prepared by stirring palladium dichloride (4.00 g, 22.6 mmol) overnight in acetonitrile (100 mL). (A few chunks of unreacted $PdCl_2$ were still usually present.) To this mixture was added silver nitrite (3.48 g, 22.6 mmol) dissolved in acetonitrile (40 mL) resulting in immediate precipitation of silver chloride. After all the chunks of $PdCl_2$ had disappeared (~1 h), the reaction mixture was filtered without difficulty and the silver chloride cake washed with acetonitrile. The solvent was evaporated from the clear orange filtrate under vacuum for ~1 h to yield nitro complex **1** (6.11 g, 100%) as a yellow to yellow-orange powder. (Prolonged exposure to the open air or vacuum leads to partial loss of acetonitrile with concomitant darkening to a deep orange. The complex is therefore best stored at 0 °C in a tightly closed bottle.) The product may be recrystallized (78% yield) by dissolving in a minimum volume of acetonitrile (50 mL), adding two volumes of diethyl ether, and chilling: mp 107–109 °C dec; IR (Nujol/Fluorolube mulls) 2988 (m, $\nu_{CH}(E)$), 2928 (m, $\nu_{CH}(A_1)$), 2769 and 2659 (w, $2\nu_{NO}$), 2329 (s, ν_{CN}), 2297 (m, $\delta_{CH} + \nu_{CC}$), 1451 (s, ν_{NO} asym), ~1410 and 1356 (m, δ_{CH}), 1335 (s, ν_{NO} sym), 1028 (m, ρ_{CH}), 952 (m, ν_{CC}), 826 (s, δ_{NO2}), 600 (m, ρ_{NO2}), 418 (w) cm^{-1}. Spectra taken in a KBr disk showed a peak near 1600 cm^{-1} believed to be due to an amide hydrolysis product of the coordinated nitrile. Anal. Calcd for $C_4H_6ClN_3O_2Pd$: C, 17.80; H, 2.24; Cl, 13.13; N, 15.56. Found: C, 17.52; H, 2.28; Cl, 13.28; N, 15.28.

$Pd(CD_3CN)_2ClNO_2$ was prepared by dissolving the corresponding protio complex in CD_3CN and evaporating the solvent: IR (Nujol/Fluorolube mulls) 2241 (m, $\nu_{CD}(E)$), 2105 (m, $\nu_{CD}(A_1)$), 2322 and 2314 (s, ν_{CN}), 1450 (s, ν_{NO} asym), 1335 (s, ν_{NO} sym), 845 (m, ρ_{CD}), 866 (m, ν_{CC}), 826 (s, δ_{NO2}), 600 (m, ρ_{NO2}) cm^{-1}.

$Pd(CH_3CN)_2Cl^{15}NO_2$ was prepared from $Pd(CH_3CN)_2Cl_2$ and $Ag^{15}NO_2$ (prepared from $Na^{15}NO_2$ (Stohler, 99% ^{15}N) and $AgNO_3$): IR (Nujol/Fluorolube mulls) 2714 and 2614 (w, $2\nu_{NO}$), 1420, (s, ν_{NO} asym), 1314 (s, ν_{NO} sym), 819 (s, ν_{NO2}), 584 (m, ρ_{NO2}), 418 (w) cm^{-1}.

^{18}O-enriched $Pd(CH_3CN)_2ClNO_2$ was prepared similarly. Thus AgN^*O_2 was prepared by exchanging $NaNO_2$ (100 mg) with $H_2{}^{18}O$ (0.5 mL, ~90° ^{18}O, Mound Laboratories) in the presence of dry Dowex 50W-X8 ion-exchange resin (50 mg) for 24 h,[32] followed by treatment with a solution of $AgNO_3$ (250 mg) in $H_2{}^{18}O$ (0.25 mL). The resulting precipitate was collected by centrifugation, washed with $H_2{}^{18}O$ (0.4 mL), and dried under vacuum to give $AgN^{18}O_2$ (146 mg, 64%). Reaction of the labeled silver salt with $Pd(CH_3CN)_2Cl_2$ then gave ^{18}O-enriched $Pd(CH_3CN)_2ClNO_2$ (isotopic content was determined to be approximately 69% ^{18}O, 4% ^{17}O, and 27% ^{16}O).[5c]

Bis(chloro(cyclooctene)nitropalladium(II)) (3d). Chloroform (2 mL) was added to a 1:1 mixture of $Pd(CH_CN)_2ClNO_2$ (33 mg, 0.12 mmol) and *cis*-cyclooctene (15 mg, 0.14 mmol). The mixture was stirred for 15 min at room temperature. A trace of solid was removed by centrifugation and the solvent evaporated from the supernatant under vacuum to give **3d** as a yellow solid (35 mg, 98%). Anal. Calcd for $C_{16}H_{28}Cl_2N_2O_4Pd_2$: C, 32.22; H, 4.74; N, 4.70. Found: C, 31.11; H, 4.51; N, 4.46.

Reaction of Ethylene with Nitro Complex 1. A solution of either nitro complex **1** or its CD_3CN analogue (~7 mg) in $CDCl_3$ (~0.5 mL) was treated with excess ethylene and monitored by ^{1}H NMR. Within 1 min of mixing, two pairs of triplets are observed, one set at 4.30 and 1.96 ppm and the other at 4.23 and 2.72 ppm. Over the next 20 min, the averaged nitrile resonance drifts upfield signifying the presence of more free nitrile and the triplet at 2.72 ppm gradually broadens and drifts downfield to 2.89 ppm. The latter also virtually disappears, together with its partner at 4.23 ppm, with a concomitant growth of the other set of triplets, the higher field partner of which drifts upfield to 1.92 ppm. The oxidation product acetaldehyde can also be seen at this point. Removal of some of the excess ethylene leads to marked broadening and a downfield shift of the ~1.9 ppm triplet and an increase in the fraction of coordinated nitrile. Further removal of ethylene results in the disappearance of the 4.30 and ~1.9 ppm triplets and reformation of the 4.23 and ~2.5 ppm triplets. The latter is very broad, however, and can appear as far upfield as 2.2 ppm. Nearly complete removal of excess ethylene causes this peak to sharpen to a clean triplet. The small residual ethylene peak is also observed to be at 5.23 ppm, *upfield* of free ethylene (5.38 ppm).

Reaction of Propylene with Nitro Complex 1. Nitro complex **1** or its CD_3CN analogue (~8 mg) was dissolved in $CDCl_3$ (0.5 mL) and treated with excess propylene. Infrared spectra taken within 2 min showed the presence of complexed propylene ($\nu_{C=C}$ = 1540 cm^{-1}). Over a period of ~20 min, metallacycle **4b** grew in ($\nu_{N=O}$ = 1628 cm^{-1}; ^{1}H NMR δ 4.55 (1 H, ~sextet, $J \approx 6$ Hz), 3.48 (1 H, d of d, $J = 4.7, 8.8$ Hz), 3.16 (1 H, d of d, $J = 6.5, 8.8$ Hz), 1.56 (3 H, d, $J = 6.3$ Hz)) until it accounted for approximately 20% of the palladium in solution. The chemical shifts of the metallacyclic protons varied by about 0.1 ppm depending on how much alkene was present. The more alkene present (and hence the more free acetonitrile present as evidenced by the nitrile chemical shift which varied from 2.15 to 2.02 ppm) the farther upfield the metallacyclic

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(32) Samuel, D.; Wassermann, I. *J. Labelled Compd.* **1971**, *7*, 355–356.

protons resonated. The oxidation product acetone could also be detected.

Reaction of Isobutylene with Nitro Complex 1, A solution of nitro complex **1** (~7 mg) in $CDCl_3$ (~0.5 mL) was treated with isobutylene and monitored by IR and ^{1}H NMR. Within time of mixing at room temperature, ~60% of the palladium was found to be present as metallacycle **4c** ($\nu_{N=O}$ = 1620 cm^{-1}; ^{1}H NMR δ 3.32 (2 H, s), 1.66 (6 H, s)). As in the case of propylene, the chemical shift of the metallacyclic protons varied by ~0.05 ppm.

Norbornene Metallacycle 4e, Norbornene (131 mg, 1.39 mmol) was added to a solution of $Pd(CH_3CN)_2ClNO_2$ (308 mg, 1.14 mmol) in acetone (15 mL). The dark orange solution became light yellow and soon deposited a bright yellow precipitate. After 5–10 min the precipitate was allowed to settle, the supernatant removed, and the solid washed with acetone (2 × 10 mL) and dried overnight under vacuum. The analytically pure, bright yellow solid (213 mg, 66%) is somewhat heat and light sensitive. Essentially quantitative yields of nearly pure material are obtained by evaporating the crude reaction mixture (in which case dichloromethane is a convenient solvent), consistent with NMR studies which show that the formation of **4e** is essentially quantitative. Attempts to recrystallize the complex only resulted in yellow powders: IR (KBr disk, intensity, shifts on ^{15}N and ^{18}O labeling, tentative idealized assignment) 2973, 2944, 2871, 1610 (vs. −31, −38, $\nu_{N=O}$), 1450, 1313 (s), 1138, 1083 (s, −2, −3), 1016 (s, −1, −6), 984 (s, 0, −7, ν_{CO}), 939, 888 (s, −1, −4), 871 (s, −1, −2), 846 (s, −2, −5), 774 (s, 0, −3), 761 (s, −4, −13, ν_{N-O}), 644 (w, −2, −5), 597 (w, 0, +12), 503 (w, −2, −13, δ_{ONO}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.37 (1 H, q, J = 5, ~1.5 Hz), 4.29 (1 H, q, J = 6, 2.5 Hz), 2.57 (1 H, s), 2.44 (1 H, br s), 1.8–1.2 (6 H, m), (C_6D_6) 3.98 (1 H, q, J = 5.5, 2.0 Hz), 3.54 (1 H, d, J = 5.7 Hz), 2.58 (1 H, s), 1.79 (1 H, s), 1.27 (1 H, d, J = 10.6 Hz), 0.93–0.48 (m, 5 H, m) ^{13}C NMR ($CDCl_3$): **4e**, δ 94.9 (d), 69.5 (d), 44.0 (d), 34.7 (t), 26.7 (t), 23.2 (t); *n*-butyl nitrite, δ 68.2, 31.2 19.2, 13.7. Anal. Calcd for $C_{14}H_{20}Cl_2N_2O_4Pd_2$: C, 29.81; H, 3.58; Cl, 12.57; N, 4.97; Pd, 37.73; M_r, 564. Found: C, 30.02; H, 3.37; Cl, 12.3; N, 5.05; Pd, 36.9; M_r, 550.

Benzonorbornene Metallacycle 4f, Complex **4f** was prepared by an analogous procedure using benzonorbornene (prepared as described in the literature).[33] The isolated complex was essentially insoluble in nondonor solvents: IR (KBr disk) 1622 cm^{-1}; ^{1}H NMR (taken quickly in Me_2SO-d_6) δ 4.62 (1 H, d, J = 5.9 Hz), 3.97 (1 H, q, J = 5.9, 2.0 Hz), 3.59 (1 H, s), 3.50 (1 H, s), 1.88 (2 H, AB quartet, $J \approx$ 10 Hz). Anal. Calcd for $C_{22}H_{20}Cl_2N_2O_4Pd_2$: C, 40.02; H, 3.06; N, 4.24. Found: C, 39.90; H, 2.86; N, 4.49.

Dicyclopentadiene Metallacycle 4g, Complex **4g** was prepared by an analogous procedure. The complex could be recrystallized from dichloromethane at −20 °C to give orange needles: IR (KBr disk) 1612 cm^{-1} (vs, $\nu_{N=O}$); ^{1}H NMR ($CDCl_3$) δ 5.65 (4 H, ~br t), 5.29 (2 H, s (CH_2Cl_2)), 4.42 (4 H, second-order AB quartet), ~3.2 (4 H, m), 2.5–1.5 (12 H, m).

Bicyclo[2.2,2]oct-2-ene Metallacycle 4h, Complex **4h** was prepared by an analogous procedure: IR (KBr disk) 1606 cm^{-1} (vs, $\nu_{N=O}$); ^{1}H NMR ($CDCl_3$) δ 4.62 (2 H, second-order AB quartet), 2.2–1.8 (2 H, m), 1.7–1.3 (8 H, m). ^{1}H NMR studies show that in the reaction of nitro complex **1** with 1 equiv of bicyclo[2.2.2]oct-2-ene the equilibrium yield of metallacycle **4h** is ~80%.

Reaction of Other Alkenes with Nitro Complex 1, The reaction of nitro complex **1** with the following alkenes was followed by NMR and shown to be qualitatively consistent with the trends reported in the Discussion: *cis*-2-butene, allylbenzene, 2-methyl-1-pentene, methylenecyclohexane, cyclopentene, cyclohexene, cycloheptene, and *cis*- and *trans*-cyclooctene. With styrene, no metallacycle could be detected.

Acrylonitrile coordinated via the nitrile functionality, methyl acrylate did not coordinate at all, while maleic anhydride did coordinate and the vinyl protons were shifted *upfield* relative to the free alkene value. 4,4-Dimethyl-2-pentene was rapidly isomerized.

X-ray Data Collection for Dicyclopentadiene Metallacycle 4g, Dichloromethane solutions of metallacycle **4g** were cooled under nitrogen to −20 °C, producing clusters of orange striated needles. Preliminary optical and X-ray diffraction studies showed that most of the crystals were twinned. Examination of several large needles under polarizing light, however, indicated that untwinned fragments might be obtained by cutting the needles lengthwise. This hypothesis was confirmed by X-ray photographs and diffractometer measurements. An untwinned crystal so obtained was glued to a glass fiber and placed on a CAD4 diffractometer with the crystallographic b^* (needle) axis approximately parallel to the ϕ goniometer axis. Since these crystals decomposed at ~15%/day in the X-ray beam at room temperature, the sample used in data collection was cooled to ~120 K in a nitrogen stream. Data for the reduced unit cell (Table III) were determined by a least-squares fit to the setting angles of 24 centered reflections (12 Friedel pairs) that sampled all octants of reciprocal space within the limits 15.0° < θ < 25.0°. The systematic extinctions observed both by photographic methods and with the diffractometer were consistent with the space group *Pbca*.

Intensity data were collected with graphite-monochromatized Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å) in the ω–2θ scan mode. Individual peak scans of θ width Δw = (0.75 + 0.35 tan θ)° plus left and right backgrounds of $^1/_4\Delta w$ were measured at rates between 0.8 and 4.0° min^{-1}, depending on the intensity levels of 4.0° min^{-1} prescans. The intensities of the (040) and (400) reflections were monitored every 2 h and did not change significantly over the course of the data collection. A total of 6140 reflections was collected, which included all accessible +*h*,+*k*,+*l* reflections between 2.0° < θ < 25.0°. The 3314 unique, nonzero observations were corrected for Lorentz, polarization, and absorption effects.[34a]

Table III. Crystallographic Data for $[Pd_2Cl_2(C_{10}H_{12}NO_2)_2]{\cdot}CH_2Cl_2$

Crystal Data

space group *Pbca*	Z = 8
a = 24.717 (6) Å	fw 725.06
b = 9.733 (2) Å	ρ_{calcd} = 1.938 g cm^{-3} (120 K)
c = 20.655 (5) Å	ρ_{obsd} = 1.95 (1) g cm^{-3} (298 K)[a]
V = 4969 (1) Å^3	T = 120 (5) K

crystal dimens: 0.09 × 0.27 × 0.04 mm
μ(Mo Kα, λ = 0.71069 Å): 18.8 cm^{-1}

Solution and Refinement Data

transmissn coeff: 0.63–0.83
no. of observns: 6140
no. of observns used in refinement (N_o): 1882 [$F_o > 3\sigma(F_o)$]
no. of variables (N_v): 168
$R_1(F_o)$ = 0.062[b]
$R_2(F_o)$ = 0.077
S = 1.17

[a] Crystal density was measured by a neutral buoyancy technique (cyclohexane/bromoform). [b] $R_1(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. $R_2(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$. Weights $w = 1/\sigma^2(F_o)$, with variances $\sigma^2(F_o) = (\sigma_c{}^2(F_o)/4F_o{}^2) + (0.04F_o)^2$ where σ_c were taken from counting statistics.

Table IV, Atomic Parameters for $[Pd_2Cl_2(C_{10}H_{12}NO_2)_2]{\cdot}CH_2Cl_2$[a]

atom	x	y	z	U_{iso}, Å^2
Pd(1)	27050 (5)	11638 (14)	12616 (5)	190 (3)[b]
Pd(2)	24504 (5)	37006 (15)	1080 (5)	184 (3)[b]
Cl(1)	3246 (2)	2663 (4)	665 (2)	237 (14)[b]
Cl(2)	1907 (2)	2229 (5)	713 (2)	239 (13)[b]
O(11)	1837 (5)	−141 (12)	1925 (5)	30 (3)
O(12)	2597 (4)	−987 (11)	2190 (5)	22 (3)
O(21)	3337 (5)	4945 (12)	−553 (5)	28 (3)
O(22)	2576 (4)	5823 (11)	−856 (5)	21 (3)
N(11)	2311 (6)	−73 (15)	1831 (6)	25 (3)
N(21)	2865 (6)	4910 (14)	−460 (6)	18 (3)
C(11)	3349 (7)	347 (17)	1684 (7)	20 (4)
C(12)	3190 (7)	−858 (16)	2123 (7)	20 (4)
C(13)	3630 (7)	1350 (20)	2158 (8)	31 (4)
C(14)	3302 (7)	1152 (19)	2793 (7)	25 (4)
C(15)	3400 (7)	−446 (17)	2794 (7)	19 (4)
C(16)	4198 (7)	762 (18)	2368 (8)	30 (5)
C(17)	4033 (7)	−512 (17)	2777 (7)	21 (4)
C(18)	4574 (8)	267 (21)	1836 (9)	39 (5)
C(19)	4565 (8)	−1242 (23)	1913 (9)	42 (5)
C(20)	4267 (9)	−1684 (21)	2413 (10)	47 (6)
C(21)	1813 (8)	4510 (18)	−344 (8)	27 (4)
C(22)	1991 (7)	5723 (16)	−758 (7)	19 (4)
C(23)	1508 (6)	3557 (16)	−815 (7)	20 (4)
C(24)	1824 (7)	3822 (19)	−1451 (8)	32 (4)
C(25)	1751 (6)	5402 (16)	−1416 (7)	16 (4)
C(26)	946 (8)	4222 (19)	−1000 (9)	37 (5)
C(27)	1127 (7)	5559 (19)	−1356 (8)	30 (4)
C(28)	614 (8)	4703 (20)	−430 (9)	38 (5)
C(29)	638 (7)	6203 (20)	−442 (8)	31 (4)
C(30)	910 (7)	6711 (17)	−973 (8)	22 (4)
C(1)	686 (9)	54 (20)	878 (16)	210 (17)[b]
Cl(3)	408 (3)	1242 (10)	428 (5)	131 (4)[b]
Cl(4)	396 (3)	−528 (12)	1572 (7)	190 (6)[b]

[a] Fractional coordinates for Pd are ×10^5, and all others are ×10^4; U_{iso} for Pd, Cl(1), and Cl(2) are ×10^4, and all others are ×10^3. [b] Equivalent U_{iso}; atom refined anisotropically.

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Structure Solution and Refinement. The direct methods program MULTAN[34b] was employed for the solution of the structure and gave the coordinates of the central core atoms (Pd_2Cl_2). Difference Fourier methods[34c] were used in locating the remaining non-hydrogen atoms and in refining the coordinates and isotropic thermal parameters of all non-hydrogen atoms. Full matrix least-squares refinement of the parameters listed in Table IV but with anisotropic thermal parameters (supplementary material) for all Pd and Cl atoms and for C(1) of the solvent gave the reliability indices listed in Table III. At this stage, a test refinement of the occupancies of the non-hydrogen atoms of the solvent molecule led to values within two esd's of 100%; full occupancies therefore were retained. Idealized positions for the 26 hydrogen atoms (C–H = 0.95 Å) were calculated and included (with B_{iso} = 4.0 $Å^2$) in the final structure factor calculation. The maximum shift/error ratio of any variable parameter in the final cycle was less than 0.1. The maximum residuals on the final difference density synthesis were ±1.2 e $Å^{-3}$ and were in the vicinity of Pd(2). An anisotropic refinement of all non-hydrogen atoms did converge ($R(F_o)$ = 0.060, N_v = 298), but the improvement in the model was not judged to be significant on the basis of Hamilton's confidence test.[35]

Atomic scattering factors and anomalous dispersion correction terms for all atoms were taken from standard tables.[36] Tables of all bond distances and angles, Pd, Cl, and C(1) anisotropic thermal parameters, fixed hydrogen atom positions, least-squares planes, and structure factors are available as supplementary material. Standard computer programs were employed in the data reduction and structure solution and refinement,[34] including Johnson's ORTEP-II for Figures 1–3.[34c]

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Registry No. **1**, 91547-45-4; **2**, 91443-56-0; **3c**, 91443-46-8; **3d**, 91443-47-9; **4a**, 91443-48-0; **4b**, 91443-49-1; **4c**, 91443-50-4; **4e**, 82135-64-6; **4f**, 91443-51-5; **4g**, 91443-52-6; **4h**, 91443-53-7; **5c**, 91443-54-8; $Pd(CD_3CN)_2ClNO_2$, 91443-44-6; $Pd(CH_3CN)_2Cl^{15}NO_2$, 91443-45-7; $Pd(CH_3CN)_2Cl_2$, 21264-30-2; $Pd(CD_3CN)_2Cl_2$, 91443-55-9; $PdCl_2$, 7647-10-1; ethylene, 74-85-1; propylene, 115-07-1; isobutylene, 115-11-7; norbornene, 498-66-8; benzonorbornene, 4486-29-7; dicyclopentadiene, 77-73-6; bicyclo[2.2.2]oct-2-ene, 931-64-6; *cis*-2-butene, 590-18-1; allylbenzene, 300-57-2; 2-methyl-1-pentene, 763-29-1; methylenecyclohexane, 1192-37-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; *trans*-cyclooctene, 931-89-5; styrene, 100-42-5; acrylonitrile, 107-13-1; maleic anhydride, 108-31-6; 4,4-dimethyl-2-pentene, 26232-98-4.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, fixed hydrogen atom positions, least-squares planes, and structure factors (17 pages). Ordering information is given on any current masthead page.

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Structure and Bonding of a Nearly Homoleptic Uranium Phoshoylide Complex

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Abstract: Golden crystals of $CpU[(CH_2)(CH_2)P(C_6H_5)_2]_3$, I, grown from diethyl ether belong to the space group $P2_1/c$ with the following unit-cell parameters: a = 14.062 (6) Å, b = 26.752 (3) Å, c = 24.220 (5) Å, β = 114.84 (2)°, V = 8268 (3) $Å^3$, Z = 8. Data collection, the solution of the structure, and refinement of the structural parameters preceeded routinely and converged at R_1 = 0.050 and R_2 = 0.060. The unit cell of I contains two nonsymmetry-related molecules IA and IB. The gross structure of both is pentagonal bipyramidal with a Cp and a CH_2 group occupying axial positions and five CH_2 moieties composing the equatorial plane. This molecule contains more actinide–carbon σ-bonding interactions than any previously characterized organoactinide complex, and they are the longest U–C σ distances, 2.66 (3) Å, yet reported. Extended Hückel molecular orbital calculations indicate significant covalent character to the U–C σ bonds in I, and an analysis of overlap populations provides an explanation for the observed structural parameters. Alternatively, the long U–C σ bonds can be rationalized in terms of an ionic bonding model.

Introduction

Phosphoylides are textbook examples of elimination stabilized alkyls that have been used to prepare homoleptic transition-metal complexes with very stable metal–carbon σ bonds.[1] As part of an ongoing investigation[2-7] of actinide–ylide chemistry, we have sought to exploit this property and have attempted the synthesis of organoactinide complexes containing many carbon–metal σ bonds.

Recently we reported[3] the synthesis of a structurally diverse and chemically interesting series of U(IV) ylide complexes.

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