

The heterobimetallic complexes **20–22** are analogous to DPPM species prepared similarly,⁶¹ and as was also noted for $[\text{RhWCl}(\text{CO})_4(\text{DPPM})_2]$, **20** is obtained as a mixture of two isomers that interconvert in solution. In contrast to the DPPM complexes, the low-temperature ³¹P NMR spectrum of **20** clearly shows two species to be present, and we presume that these are **20a** and **20b** as suggested by the X-ray results. We further suggest that these are likely to be the structure adopted for the DPPM complexes as well. Both **21** and **23** are luminescent at low temperature. Details of these results will be reported separately.

[Bis(diphenylphosphino)methyl]-2-pyridine (P_2N) behaves as a tridentate ligand on reaction with $[\text{M}(\text{CO})_3(\text{CHT})]$ ($\text{M} = \text{Mo}, \text{W}$) even when an excess of the ligand is used, and while the pyridyl group can be displaced by carbon monoxide, no reaction appears to occur with more P_2N even under forcing conditions. Attempts to prepare a heterobimetallic complex from $[\text{Rh}(\text{P}_2\text{N})_2]\text{OTf}$ and $[\text{Mo}(\text{CO})_3(\text{CHT})]$ were unsuccessful. The only identifiable species in the reaction mixture were the starting rhodium complex and **23**, implying redistribution of the ligand occurred.

Conclusion

Although the ligands $\text{CH}_3\text{N}(\text{P}(\text{OR})_2)_2$ ($\text{R} = \text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{CH}_2-$) do form dimeric complexes with group VI metals, these are homometallic. Only when $\text{R} = \text{CH}(\text{CH}_3)_2$ can substantial amounts of monomeric species suitable for forming heterobimetallic complexes be obtained. These appear not to be particularly reactive toward small molecules, presumably because of the bulk of the ligands.

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Supplementary Material Available: Figures S1–S3 and tables of bond distances, interbond angles, anisotropic thermal parameters, amplitudes of anisotropic thermal displacement, calculated hydrogen atom positions, and torsion angles for **12**, **16**, **20**, **21**, and **27** (63 pages); tables of observed and calculated structure factors for **12**, **16**, **20**, **21**, and **27** (151 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Five-Coordinate Olefin Complexes of Palladium(II). Molecular Structure of the Acetone Solvate of (2,9-Dimethyl-1,10-phenanthroline)(maleic anhydride)methylchloropalladium

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Five-coordinate olefin complexes of palladium(II) of general formula $\text{PdClMe}(\text{N-N}')(\eta^2\text{-olefin})$ have been prepared by reaction of the dimeric complex $[\text{PdClMe}(\text{Me}_2\text{S})]_2$ with planar sterically crowded nitrogenous bidentate ligands and the appropriate olefin. The X-ray crystal structure of the complex having $\text{N-N}' = 2,9\text{-dimethyl-1,10-phenanthroline}$ and olefin = maleic anhydride has been determined. This crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 7.085(2) \text{ \AA}$, $b = 15.880 \text{ \AA}$, $c = 19.062 \text{ \AA}$, $\beta = 96.79(5)^\circ$, and $Z = 4$. Refinement converged at $R = 0.024$ ($R_w = 0.026$), and the geometry of the five-coordinate palladium is trigonal bipyramidal, with the olefinic double bond in the equatorial plane and the chloride and methyl ligands in apical positions. The stability and structural and NMR spectroscopic properties of the complexes are discussed in comparison with those of analogous Pt(II) derivatives and point to a relevant contribution of π -back-donation to the Pd-olefin bond in the five-coordinate species.

Introduction

In spite of the large number of synthetic reactions involving Pd(II) mono(olefin) complexes,¹ only a limited number of species have been isolated and well characterized.^{2,3} Among these, a series of remarkably stable com-

pounds of the type $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)\text{L}(\eta^2\text{-olefin})]\text{X}$ are the only known example of coordinatively saturated species, which could be considered as formally five-coordinate.³

During the last few years, a series of contributions from our laboratories has dealt with the synthesis, structural characterization, and properties of five-coordinate olefin complexes of platinum(II),^{4–6} giving special attention to

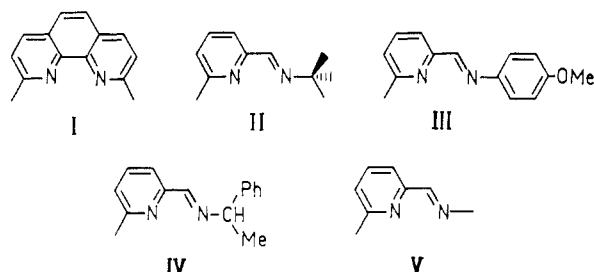
(1) Collman, J.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Most of the isolated square-planar 16e species belong to the class of the Kharasch complexes $[\text{PdCl}_2(\text{olefin})]_2$. See for example: Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 1, p 106.

(3) (a) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996. (b) Miki, K.; Shiotani, O.; Kai, Y.; Kasai, N.; Kanatani, H.; Kurosawa, H. *Organometallics* **1983**, *2*, 585. (c) Kurosawa, H.; Asada, N.; Urabe, A.; Emoto, M. *J. Organomet. Chem.* **1984**, *272*, 321.

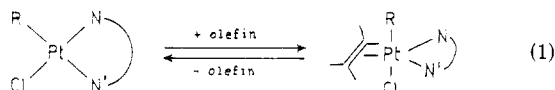
(4) (a) De Renzi, A.; Panunzi, A.; Saporito, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1977**, *107*, 549. (b) De Renzi, A.; Di Blasio, B.; Saporito, A.; Scalone, M.; Vitagliano, A. *Inorg. Chem.* **1980**, *19*, 960. (c) Albano, V. G.; Demartin, F.; De Renzi, A.; Morelli, G.; Saporito, A. *Inorg. Chem.* **1985**, *24*, 2032.

(5) (a) Albano, V. G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1987**, *6*, 517. (b) Albano, V. G.; Castellari, C.; Morelli, G.; Vitagliano, A. *Gazz. Chim. Ital.* **1989**, *119*, 235.

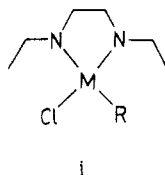
Chart I^a

^a a, CH₂=CH₂; b, CH₂=CHMe; c, CH₂=CHO-*n*-Bu; d, CH₂=CHCH₂OH; e, (Z)-HOCH₂CH=CHCH₂OH; f, CH₂=CHCOOMe; g, CH₂=CHCHO; h, CH₂=CHCN; i, (E)-NCCH=CHCN; j, maleic anhydride; k, 1,5-cyclooctadiene.

the factors affecting the stability of these species.^{4c,6} In particular it was found that four-coordinate complexes of the type PtClR(N-N') (R = alkyl or aryl, N-N' = planar bidentate nitrogen ligand) were able to coordinate a wide number of olefins in a fifth position (eq 1), provided the



nitrogen ligand was crowded on both sides, in such a way as to destabilize the square-planar arrangement (i) by steric



interactions with the Cl and R ligands.⁶ On the basis of these results, we argued that the same effect could help in stabilizing⁷ five-coordinate olefin complexes of palladium(II), which were unknown (with the possible exception of the above-cited cyclopentadienyl species). We explored the possibilities of preparing complexes of the general formula PdXR(N-N')(olefin), by using N-N' ligands having the above-mentioned steric requirements, and we report in this paper the synthesis and characterization of a number of complexes of the type PdClMe(N-N')(η²-olefin), together with the molecular structure of PdClMe(2,9-Me₂-1,10-phen)(MA) (2,9-Me₂-1,10-phen = 2,9-dimethyl-1,10-phenanthroline; MA = maleic anhydride). Some preliminary results concerning the preparation of the complexes appeared in a previous communication.⁸

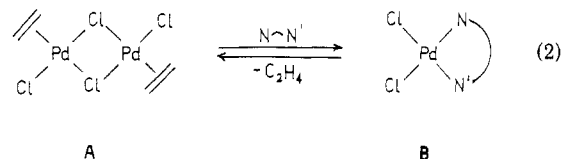
Results and Discussion

Choice of the Ligands. We chose as suitable ligands the diimines I-V (Chart I) which had been previously used in the investigation of Pt(II) five-coordinate olefin complexes.⁶ Ligands I and II had been shown to give the most stable PtClMe(N-N')(C₂H₄) complexes,⁶ the rigid structure of I increasing both the stability toward olefin dissociation and the stability toward the dissociation of one^{4c} or both nitrogen atoms. Ligand III had given complexes in the medium-high range of stability, and the olefin dissociation

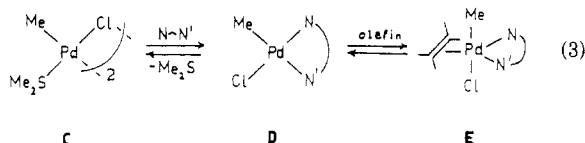
constants of its complexes had been measured for a wide series of olefins.⁶ Therefore, it could be especially useful for getting direct quantitative comparisons between analogous platinum and palladium species. The unsymmetrical and chiral ligand IV had been used to resolve a chiral bipyramidal platinum center^{5a} and could be of interest for the same purpose in the palladium case. Ligand V, whose structure only partly matches the favorable skeleton i,⁶ had given an ethylene complex of medium-low stability, and it was chosen to confirm the trend in the case of palladium complexes.

Synthesis and Characterization of the Complexes.

Our first attempt to obtain a five-coordinate palladium complex was the reaction of the chloride-bridged dimer A (analogous to Zeise's dimer) with 2,9-dimethyl-1,10-phenanthroline (I), according to eq 2. Although this is



a common way to prepare Pt(II) five-coordinate complexes,⁴ no such species was obtained in the case of palladium, the dichloride B being produced instead. Even when the reaction was performed in a NMR tube at -40 °C, no intermediate five-coordinate species could be detected, and the formation of B with ethylene loss was directly observed. After that, we used the chloride-bridged methyl complex C⁹ as starting material, and we succeeded in preparing five-coordinate complexes according to eq 3.



The olefin coordination-dissociation equilibrium depicted in eq 3 is thus perfectly analogous to that found for Pt(II) complexes.^{5a,6} The synthesis was generally performed at -30 °C either in two separate steps, by first isolating the intermediate PdClMe(N-N') complex (ligands I, III and IV), or in a single step, through an olefin-assisted displacement reaction (ligand II). In the case of ligand V, no appreciable amounts of five-coordinate species were detected at room temperature with any of the olefins a-i. We note that the olefin exchange reaction on complexes E is usually fast, and therefore a complementary synthetic procedure can be the olefin exchange on an already formed ethylene complex.

All the complexes we have isolated were characterized by elemental analysis, conductivity measurements, ¹H NMR spectroscopy (200 or 270 MHz), and, in some cases, IR and ¹³C NMR spectroscopy. Some of the complexes were not isolated, owing to easy decomposition, and were only identified through the ¹H NMR spectra of the crude solutions. Selected NMR data are reported in Table I, together with the numbering of the compounds.

Besides the analytical and conductivity data (with the exception of 1k⁺ the complexes are not conducting in chloroform), the assignment of a five-coordinate structure to complexes E was made on the basis of ¹H and ¹³C (when available) NMR data and was ultimately confirmed by the X-ray diffraction analysis of 1j. Particularly relevant for the structural assignment is the observation of chemical

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(7) Unless otherwise stated, throughout this paper the terms "stability" and "stable complex" refer to the thermodynamic stability of a five-coordinate complex toward olefin dissociation.

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Table I. Selected ^1H NMR Data (δ [^{13}C δ in Brackets]) for $\text{PdClMe}(\text{N-N}')(\text{olefin})$ and $\text{PdClMe}(\text{N-N}')(\text{N-CMe})$ Complexes^a

no.	complex	Pd-Me	N-CMe (heteroarom)	HC=CH ^b (olefinic)	other selected signals
1	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})^c$	1.10	3.08		7.58 (d, 2 H), 7.77 (2 H), 8.24 (d, 2 H)
1a	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{C}_2\text{H}_4)^d$	0.34 [7.8]	3.36 [28.0]	3.52 (d, 2 H), ^e 4.36 (d, 2 H) ^e [61.3]	7.73 (d, 2 H), 7.83 (2 H), 8.29 (d, 2 H)
1b	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{CH}_2=\text{CHMe})^f$	0.26	3.35, 3.40	3.55 (d, 1 H), 4.1 (m, 2 H)	1.96 (d, =CMe)
1b	as above, rotamer, 40% abund ^f	0.34	3.33, 3.45	4.50 (d, 1 H), 5.19 (m, 1 H)	1.59 (d, =CMe)
1c	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{CH}_2=\text{CHO}-n\text{-Bu})^{g,h}$	0.32 [11.2]	3.25, 3.53 [27.0, 29.6]	3.20 (d, 1 H), 6.83 (dd, 1 H) [47.0 (CH ₂), 115.7 (CH)]	
1d	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{CH}_2=\text{CHCH}_2\text{OH})^{f,i}$	0.44 [8.9]	3.33, 3.38 [27.4, 28.2]	4.0–4.5 (m, 3 H) [59.1 (CH ₂), 81.2 (CH)]	4.60 (d, CH ₂ OH)
1e	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})((Z)\text{-HOCH}_2\text{CH}=\text{CHCH}_2\text{OH})$	0.62	3.33	4.27 (m, 2 H)	4.32 (dd, 2 CHOH), 4.77 (dd, 2 CHOH)
1f	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{CH}_2=\text{CHCOOMe})$	0.56 [15.4]	3.24, 3.31 [27.9, 28.1]	3.99 (d, 1 H), 4.51 (d, 1 H), 5.30 (dd, 1 H) [60.9 (CH ₂), 64.4 (CH)]	3.60 (OMe), 7.67 (d, 2 H), 7.77 (2 H), 8.23 (d, 1 H), 8.25 (d, 1 H)
1g	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{CH}_2=\text{CHCHO})^j$	0.67	3.16, 3.37	3.98 (d, 1 H), 4.13 (m, 1 H), 4.84 (d, 1 H)	7.72 (d, 1 H), 7.75 (d, 1 H), 7.84 (2 H), 8.3 (d, 1 H), 8.34 (d, 1 H), 9.9 (d, CHO)
1h	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{CH}_2=\text{CHCN})$	0.97 [18.8]	3.24, 3.37 [27.8, 28.4]	3.67 (d, 1 H), 4.47 (d, 1 H), 4.68 (dd, 1 H) [60.7 (CH ₂), 42.7 (CH)]	7.74 (d, 1 H), 7.77 (d, 1 H), 7.84 (2 H), 8.33 (d, 2 H)
1i	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})((E)\text{-NCCH}=\text{CHCN})$	1.27 [−4.5]	3.31, 3.32 [28.3, 28.7]	3.87 (d, 1 H), 4.91 (d, 1 H) [41.5, 42.3]	7.82 (d, 2 H), 7.92 (2 H), 8.42 (d, 2 H)
1j	$\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{MA})$	1.06	3.25	5.60 (2 H)	7.83 (d, 2 H), 7.91 (2 H), 8.41 (d, 2 H)
1k ⁺	$[\text{PdMe}(\text{2,9-Me}_2\text{-1,10-phen})(1,5\text{-COD})]$	1.14 [12.3]	3.38 [27.5]	4.68 (m, 2 H), 5.08 (m, 2 H) [85.1, 126.3]	7.96 (d, 2 H), 8.00 (2 H), 8.52 (d, 2 H)
2a	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{N-}t\text{-Bu})(\text{C}_2\text{H}_4)$	0.30	3.05	3.32 (d, 2 H), ^d 4.17 (d, 2 H) ^d	7.47 (d, 2 H), 7.83 (t, 1 H), 8.40 (N=CH)
2h	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{N-}t\text{-Bu})(\text{CH}_2=\text{CHCN})$	0.90	3.08	3.49 (d, 2 H), 4.30 (d, 2 H), 4.55 (dd, 1 H)	1.66 (CMe ₃), 8.47 (N=CH)
2h	as above, diastereomer, 35% abund	0.95	2.96	3.52 (d, 2 H), 4.41 (d, 2 H), 4.55 (dd, 1 H)	1.65 (CMe ₃), 8.45 (N=CH)
3	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})$	0.90	3.05		3.81 (OMe), 8.41 (N=CH)
3a	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})(\text{C}_2\text{H}_4)^{g,h}$	0.25	3.07	3.3 (br, 1 H), 3.5 (br, 1 H), 4.3 (br, 2 H)	3.86 (OMe), 8.70 (N=CH)
3i	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})((E)\text{-NCCH}=\text{CHCN})^g$	1.20	3.06	3.61 (d, 1 H), 4.85 (d, 1 H)	3.85 (OMe), 8.67 (N=CH)
3i	as above, diastereomer, 40% abund	1.29	3.06	<i>j</i> , 4.78 (d, 1 H)	3.85 (OMe), 8.70 (N=CH)
4	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{N-(S)-CH(Me)Ph})$	1.27	3.00		1.70 (d, Me), 5.34 (q, N=CH), 8.06 (N=CH)
4a'	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{N-(S)-CH(Me)-Ph})(\text{C}_2\text{H}_4)^{g,h}$	−0.24	2.98	3.10 (m, 1 H), 3.21 (m, 1 H), 4.18 (m, 2 H)	2.08 (d, Me), 5.16 (q, N=CH), 8.45 (N=CH)
4a''	as above, diastereomer, 30% abund ^{g,h}	0.06	3.02	<i>j</i>	2.00 (d, Me), 5.38 (q, N=CH), 8.17 (N=CH)
5	$\text{PdClMe}(\text{6-Mepy-2-CH}=\text{NMe})$	1.21	2.97		3.50 (NMe), 8.42 (N=CH)

^a 270 or 200 MHz [67.9 or 50.3 MHz for ^{13}C]; in CDCl_3 . Abbreviations: d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak; no attribute, singlet. Fine structure due to long-range coupling ($J < 2$ Hz) is ignored. ^b Olefinic ^{13}C chemical shifts of selected free olefins are as follows: **a**, 116.6; **c**, 85.7, 151.7; **d**, 115.0, 137.4; **f**, 130.7, 125.7; **h**, 137.4, 125.8; **i**, 119.3; **m**, 128.7. For α -olefins, the first value refers to the $=\text{CH}_2$ carbon. ^c The halves of the dimethylphenanthroline ligand appear to be equivalent, indicating fast site exchange of the Cl and Me ligands. The equivalence disappears below -40°C .⁸ ^d Spectrum was recorded at 0°C , to freeze dynamic behavior. ^e Pseudodoublets, actually constituting a AA'XX' of more complex multiplet. ^f Spectrum was recorded at -20°C , to avoid dissociation and freeze dynamic behavior. ^g This complex is extensively dissociated at room temperature and was not isolated. Spectrum was recorded in presence of excess free olefin. ^h Spectrum was recorded at -40°C , to avoid dissociation and freeze dynamic behavior. ⁱ A second diastereomer is detectable, in less than 10% abundance. ^j Signals overlapped by those of the major isomer.

equivalence for the halves of ligand I in the case of the complexes with olefins having a mirror plane bisecting the double bond (**1a,e,j**). This equivalence disappears when olefins lacking such symmetry are bound to the metal (**1b,d,f-i**).

It is important to note that, whenever olefins other than ethylene are coordinated, different diastereomers can be

formed, depending on the symmetry of the olefinic and N-N' ligands. For example two isomers are possible (and they are actually observed) for the complex $\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{CH}_2=\text{CHMe})$ (**1b**). In many cases one of the isomers is largely predominant (see Table I). A special case is that of the complex $\text{PdClMe}(\text{6-Mepy-2-CH}=\text{N-(S)-CH(Me)Ph})(\text{C}_2\text{H}_4)$ (**4a**), which consists of a 7:3 equi-

Table II. Olefin Dissociation Constants ($T = 33^\circ\text{C}$) for $\text{MClMe}(\text{N-N}')(\text{olefin})$ Complexes

compd	N-N'	olefin	pK_{diss}	
			M = Pd	M = Pt ^a
1a	2,9-Me ₂ -1,10-phen	CH ₂ =CH ₂	2.5	7 ^b
1b		CH ₂ =CHMe	0.4	5 ^b
1c		CH ₂ =CHO- <i>n</i> -Bu	-0.7 ^c	4 ^b
1d		CH ₂ =CHCH ₂ OH	1.9	6 ^b
1e		(<i>Z</i>)-HOCH ₂ CH=CHCH ₂ OH	1.0	
1f		CH ₂ =CHCOOMe	1.2	6 ^b
1g		CH ₂ =CHCHO	2.3	7 ^b
1h		CH ₂ =CHCN	2.6	8 ^b
3a	6-Mepy-2-CH=NC ₆ H ₄ OMe	CH ₂ =CH ₂	0.2 ^c	3.7
3i		(<i>E</i>)-NCCH=CHCN	0.4	7 ^b
4a	6-Mepy-2-CH=NCH(Me)Ph	CH ₂ =CH ₂	-0.1 ^c	3.1

^a Data from ref 6. ^b Estimated values.⁶ ^c Extrapolated from three measurements made at lower temperatures.

librium mixture of two diastereomers differing in the configuration of the chiral palladium center. The most abundant diastereomer (**4a'**) is strictly analogous to the previously isolated^{5a} platinum complex $\text{C-PtClMe}(6\text{-Mepy-2-CH=N-(S)-CH(Me)Ph})(\text{C}_2\text{H}_4)$, whose absolute configuration was determined by X-ray crystallography.^{5a} Owing to extensive dissociation at room temperature (see Table II), **4a** was not isolated, being characterized through its ¹H NMR spectrum in the equilibrium mixture with the corresponding four-coordinate complex **4** and free ethylene at temperatures below 0°C ($pK_{\text{diss}} = 2.0$ at -55°C).

We observed that, in contrast with the case for square-planar complexes,¹⁰ the exchange between free and coordinated olefin is quite slow on the NMR time scale, in good agreement with the results reported for the other coordinatively saturated Pd(II) olefin complexes so far described.³ Moreover, an unprecedented slow rotation of the olefin around the Pd-olefin axis is observed for complexes of ligand I. The rotation becomes more hindered for complexes of electron-withdrawing olefins. Thus, for example, the 200-MHz ¹H NMR spectrum of **1a**, recorded at 25°C , displays two broad doublets for the ethylene protons, centered at $\delta = 4.4$ and 3.5 , respectively, which become sharp pseudodoublets ($\delta = 4.36$ and 3.52) at 0°C .¹¹ In the case of the fumarodinitrile complex **1i**, sharp signals from the two diastereotopic olefinic protons and from protons belonging to the nonequivalent halves of the dimethylphenanthroline ligand are observed up to 50°C .¹²

Another relevant feature of the NMR spectra, which closely parallels the spectral properties of analogous Pt(II) complexes, is the large upfield shift observed for the proton and carbon olefinic resonances compared with the signals for the free molecules. The upfield shift $\Delta\delta$ observed upon coordination is 1–2 ppm for ethylene protons and ~ 55 ppm for ethylene carbons (compare with the average values of 2–3 ppm and ~ 85 ppm for platinum complexes).^{5a,6} Higher coordination shifts are observed for olefins bearing electron-withdrawing substituents (see Table I). This large upfield shift was found to be diagnostic of olefin coordi-

nation in a bipyramidal Pt(II) complex^{4c,5a,6,13} and was also observed for the coordinatively saturated Pd(II)-olefin complexes $[\text{Pd}(\text{C}_5\text{H}_5)(\text{L})(\text{olefin})]^+$ cited above.^{3a} It is interesting to note that in the case of square-planar Pd(II) olefin complexes the opposite trend was observed for proton shifts,^{10b,14} and a much lower upfield shift was observed for carbon resonances.¹⁵ These observations suggest that a large upfield shift of olefinic protons and carbons can generally be considered as strong evidence of five-coordination for Pd(II) complexes as well as for Pt(II) species.

If the correlation¹⁶ between the upfield shift of olefinic protons and carbons and the extent of π -back-donation is valid,¹⁷ the above-mentioned upfield shifts suggest a relevant contribution of π -back-donation in the five-coordinate species, which is not found in square-planar complexes,¹⁹ in agreement with previous suggestions based on thermodynamic and structural observations on $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\eta^2\text{-olefin})]^+$ complexes.^{3b} As expected, this contribution appears to be smaller for palladium than for platinum species, the upfield coordination shifts for complexes **E** being about two-thirds of those observed for the corresponding Pt(II) complexes. This is in agreement with the results concerning the stability of the complexes, which are reported in the following section. The extent of π -back-donation, as evidenced by the NMR coordination shifts, appears thus to be strongly dependent on the coordination number. Moreover, as could be expected from molecular orbital considerations,²⁰ the π -back-donation also depends on the coordination position occupied by the olefinic double bond. A clear example of this effect is given by the ¹³C NMR spectra of the two complexes $[\text{PdMe}(\text{1,5-COD})(2,9\text{-Me}_2\text{-1,10-phen})]^+$ (**1k**⁺) and $[\text{PtMe}(\text{1,5-COD})(2,9\text{-Me}_2\text{-1,10-phen})]^+$ ^{21a} (1,5-COD = 1,5-cyclooctadiene), which both contain two differently coordinated double bonds, in equatorial and axial positions, respectively. While the ¹³C chemical shifts for the equatorially coordinated double bonds fall in the range expected for five-coordinate complexes ($\Delta\delta = 43$ ppm in **1k**⁺ and $\Delta\delta = 71$ ppm in the platinum derivative), the coordination shifts for the axially coordinated double bond are much lower ($\Delta\delta = 2$ ppm in **1k**⁺ and $\Delta\delta = 11$ ppm in the platinum derivative). Even if part of the above effect can be ascribed to the high donor power and trans influence of the methyl group,²² this constitutes strong evidence for the role of the

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(17) This more or less intuitive idea is probably only partially correct.¹⁸ Nevertheless, at least two combined observations are in good agreement with it: first, olefins bearing electron-withdrawing substituents give more stable five-coordinate Pt(II) complexes;⁶ second, these species display larger ¹³C coordination shifts, $\Delta\delta$. For example, the olefinic carbons in the complex $\text{PtClMe}(2,9\text{-Me}_2\text{-1,10-phen})(\text{dimethyl fumarate})$ display a coordination shift $\Delta\delta$ of -101 ppm, while this is -87 ppm in the corresponding ethylene complex. This trend appears to be general (Cucciolito, M. E.; De Felice, V.; Vitagliano, A. Unpublished results. See also ref 3). Thus, chemical evidence (increased bond strength for olefins that are supposed to favor π -back-donation) parallels spectroscopic evidence (larger ¹³C coordination shifts for these olefins).

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(11) In the previously cited coordinatively saturated complexes $[\text{Pd}(\text{C}_5\text{H}_5)(\text{L})(\text{olefin})]^+$, free rotation about the metal-olefin axis was observed at temperatures down to -80°C .^{3a}

(12) The temperature was not raised further to avoid decomposition.

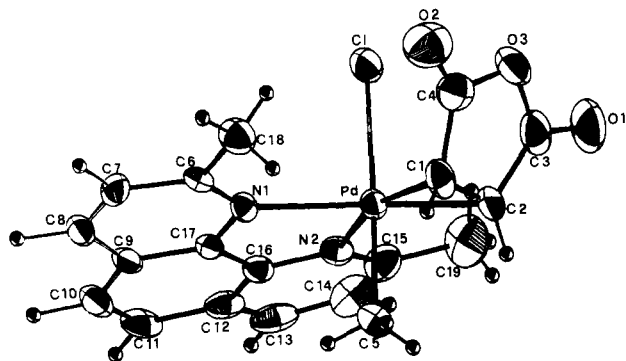


Figure 1. Thermal ellipsoid plot of $[\text{PdCl}(\text{CH}_3)(\text{C}_4\text{H}_2\text{O}_3)(\text{C}_{14}\text{H}_{12}\text{N}_2)]$ with non-hydrogen atoms drawn at the 50% probability level and hydrogen atoms drawn artificially small.

coordination geometry in determining the extent of π -back-donation.

Olefin Dissociation Equilibria and Comparison with Pt(II) Species. We have investigated the olefin dissociation equilibria for some of the complexes. The dissociation pK 's in CDCl_3 solution were determined through the ^1H NMR analysis of equilibrium mixtures of four- and five-coordinate species containing an excess of free olefin, by using essentially the same procedure already described for Pt(II) complexes.⁶ Since at least some of the ^1H NMR signals were unambiguously assignable to the four- or to the five-coordinate species and since the olefin exchange rate was very slow on the NMR time scale, integration of the signals gave a direct measure of the relative concentrations. The measurements were made at 33 °C, in order to make possible a direct comparison with the data previously reported for Pt(II) complexes, and the results are reported in Table II, together with the corresponding values (measured or estimated⁶) referring to platinum complexes.

Even if the data reported in Table II are limited in number and accuracy, nevertheless some general conclusions can confidently be drawn.

(1) Palladium complexes are less stable than platinum complexes by about 4 orders of magnitude (pK difference in the range 3–5). For this reason the number of isolable complexes is much lower with Pd than with Pt, being limited to the N-N' ligands with a very large five-coordination-stabilizing effect (e.g. I).

(2) The effect of the nitrogen bidentate ligands on the stability of the complexes closely parallels that observed for Pt(II), thus confirming the role of steric factors in stabilizing the trigonal-bipyramidal geometry (for a full discussion see ref 6).

(3) Electron-withdrawing substituents on the olefinic double bond increase the stability of the complexes. This effect is much lower than for Pt(II) complexes (see Table II) and is partially or totally balanced by the steric hindrance of the substituents, which acts in the opposite direction. The relatively high stability of five-coordinate species containing electron-withdrawing olefins provides chemical evidence of the important role of π -back-donation in these complexes, thus confirming the NMR spectroscopic evidence already discussed in the previous section.

Molecular Structure of $\text{PdClMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{MA})$ (1j). The structure of the title compound is shown in Figure 1 and is the first report of a Pd(II) trig-

Table III. Fractional Atomic Coordinates

atom	x	y	z
Pd	0.29967 (5)	0.13198 (3)	0.18884 (2)
Cl	0.58931 (17)	0.20597 (10)	0.15843 (6)
N(1)	0.4692 (5)	0.0180 (3)	0.2085 (2)
N(2)	0.2725 (5)	0.0683 (3)	0.0853 (2)
O(1)	0.1844 (7)	0.3643 (3)	0.1356 (3)
O(2)	0.4799 (6)	0.2839 (3)	0.3440 (2)
O(3)	0.3627 (6)	0.3398 (3)	0.2390 (2)
C(1)	0.2277 (7)	0.2122 (4)	0.2689 (2)
C(2)	0.1332 (6)	0.2382 (4)	0.2032 (3)
C(3)	0.2203 (8)	0.3190 (5)	0.1851 (3)
C(4)	0.3722 (8)	0.2772 (5)	0.2905 (3)
C(5)	0.0759 (7)	0.0611 (3)	0.2138 (2)
C(6)	0.5839 (7)	-0.0016 (4)	0.2676 (2)
C(7)	0.6779 (8)	-0.0793 (5)	0.2736 (3)
C(8)	0.6529 (8)	-0.1373 (4)	0.2206 (3)
C(9)	0.5354 (7)	-0.1182 (4)	0.1577 (3)
C(10)	0.5078 (8)	-0.1744 (4)	0.0981 (3)
C(11)	0.4098 (8)	-0.1479 (5)	0.0372 (3)
C(12)	0.3305 (7)	-0.0658 (5)	0.0296 (2)
C(13)	0.2415 (7)	-0.0332 (5)	-0.0350 (2)
C(14)	0.1743 (7)	0.0463 (5)	-0.0380 (2)
C(15)	0.1889 (6)	0.0973 (4)	0.0238 (2)
C(16)	0.3443 (7)	-0.0115 (4)	0.0884 (2)
C(17)	0.4514 (6)	-0.0388 (4)	0.1539 (2)
C(18)	0.6046 (7)	0.0611 (4)	0.3251 (3)
C(19)	0.1153 (7)	0.1843 (4)	0.0219 (2)
O(4)	0.9256 (9)	-0.1088 (4)	0.5925 (3)
C(20)	0.8762 (11)	-0.1108 (5)	0.5297 (4)
C(21)	1.0192 (13)	-0.1155 (6)	0.4771 (4)
C(22)	0.6688 (13)	-0.1126 (7)	0.5008 (6)

onal-bipyramidal complex. The molecule is structurally very similar to the octahedral Pd(IV) complex $\text{PdIme}_3(\text{bpy})$ ²³ ($\text{bpy} = 2,2'$ -bipyridine). This raises the question, as always in the case of metal-olefin complexes (see for instance ref 1, p 41), if the metal-olefin bond could be alternatively considered as a Pd(IV) metallacycle. The geometrical parameters (vide infra) of the coordinated maleic anhydride molecule indicate a structure intermediate between these two limiting bonding models. When π -back-bonding contributions are taken into account, the former representation seems to be more appropriate to the chemical properties of this class of compounds (e.g. the reversibility of the olefin coordination), especially in the case of ethylene and olefins not bearing electron-withdrawing substituents.

The crystal contains discrete molecules of the complex and clathrated acetone in a 1:1 molar ratio. The refined atomic parameters are listed in Table III, and relevant bond lengths and angles are reported in Table IV. The palladium atom exhibits a trigonal-bipyramidal coordination geometry with the chloride and methyl ligands in axial positions. The bidentate N-N' ligand and the alkene double bond of the maleic anhydride define the equatorial plane. The anhydride group of the maleic anhydride is oriented toward the chloride ligand. The idealized molecular symmetry is C_s . The coordination geometry strictly resembles that of the platinum(II) complexes having similar chemical composition and geometry such as $\text{PtClIme}(\text{6-Mepy-2-CH=N-(S)-CH(Me)Ph})$,^{5a} $\text{PtCl}(\text{CH}(\text{CH}_2)_2\text{CH=CH}(\text{CH}_2)_2\text{CH(OMe)})(\text{2,9-Me}_2\text{-1,10-phen})$,^{5b} and $[\text{PtMe}(\text{2,9-Me}_2\text{-1,10-phen})(\text{C}_2\text{H}_4)(\text{MeCN})](\text{BF}_4)$.²¹ A comparison of the palladium-ligand distances with the corresponding platinum-ligand values is reported in Table V. The table does not give unequivocal evidence of differences between the atomic radii of the two metals because electronic and steric factors affect the metal-ligand distances more than the expected difference in atomic

(22) In the square-planar complex $\text{PtClIme}(\text{1,5-COD})$ the coordination shifts $\Delta\delta$ for the olefinic carbons are 45 ppm for the carbon cis to the methyl group and 16 ppm for the one trans: Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; Ward, J. E. *H. J. Am. Chem. Soc.* **1975**, *97*, 721.

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Table IV. Interatomic Distances (Å) and Relevant Angles (deg), with Standard Deviations in Parentheses, of [PdCl(CH₃)(C₄H₂O₃)(C₁₄H₁₂N₂)]•(CH₃)₂CO

Pd-Cl	2.492 (1)	C(15)-C(19)	1.476 (9)
Pd-C(5)	2.046 (5)	C(6)-C(7)	1.400 (9)
Pd-N(1)	2.181 (4)	C(15)-C(14)	1.423 (8)
Pd-N(2)	2.206 (4)	C(7)-C(8)	1.363 (9)
Pd-C(1)	2.097 (5)	C(14)-C(13)	1.348 (9)
Pd-C(2)	2.095 (6)	C(8)-C(9)	1.410 (8)
C(1)-C(2)	1.410 (7)	C(13)-C(12)	1.414 (7)
C(1)-C(4)	1.478 (9)	C(9)-C(10)	1.440 (9)
C(2)-C(3)	1.481 (9)	C(12)-C(11)	1.420 (9)
C(3)-O(1)	1.190 (8)	C(9)-C(17)	1.391 (9)
C(4)-O(2)	1.204 (7)	C(13)-C(16)	1.409 (8)
C(3)-O(3)	1.392 (7)	C(10)-C(11)	1.348 (8)
C(4)-O(3)	1.392 (8)	C(17)-C(16)	1.449 (6)
C(1)-H(1)	0.91 (4)	C(17)-N(1)	1.372 (7)
C(2)-H(2)	0.91 (2)	C(16)-N(2)	1.363 (9)
N(1)-C(6)	1.345 (6)	O(4)-C(20)	1.206 (8)
N(2)-C(15)	1.332 (6)	C(20)-C(21)	1.51 (1)
C(6)-C(18)	1.476 (8)	C(20)-C(22)	1.51 (1)
Cl-Pd-C(5)	174.7 (2)	C(6)-C(7)-C(8)	121.5 (4)
N(1)-Pd-N(2)	76.2 (2)	C(13)-C(14)-C(15)	120.5 (5)
C(1)-Pd-C(2)	39.3 (2)	N(1)-Pd-C(5)	86.0 (2)
N(1)-Pd-C(1)	123.8 (2)	N(2)-Pd-C(5)	88.2 (2)
N(2)-Pd-C(2)	119.7 (2)	C(1)-Pd-C(5)	84.4 (2)
Pd-C(2)-C(3)	114.2 (4)	C(2)-Pd-C(5)	87.0 (2)
Pd-C(1)-C(4)	114.0 (4)	N(1)-Pd-Cl	88.8 (1)
C(1)-C(4)-O(2)	130.3 (6)	N(2)-Pd-Cl	89.7 (1)
Pd-N(1)-C(6)	127.0 (4)	C(1)-Pd-Cl	99.2 (2)
Pd-N(2)-C(15)	127.7 (4)	C(2)-Pd-Cl	98.2 (2)
Pd-N(1)-C(17)	114.6 (3)	C(2)-C(3)-O(1)	130.7 (5)
Pd-N(2)-C(16)	113.2 (3)	C(1)-C(4)-O(3)	109.2 (4)
C(7)-C(6)-C(18)	122.0 (5)	C(2)-C(3)-O(3)	108.6 (5)
C(14)-C(15)-C(19)	121.3 (5)	C(3)-O(3)-C(4)	108.7 (5)

Table V. Comparison of the Palladium-Ligand Distances (Å) with the Corresponding Platinum-Ligand Values in Similar Complexes

com- plex ^a	M-C(alkyl)	M-Cl	M-C(olefin)	M-N
a	2.046 (5)	2.492 (1)	2.096 (5)	2.194 (5) (Me ₂ phen)
b	2.055 (6)	2.457 (2)	2.053 (6)	2.188 (4) (imine), 2.239 (5) (py)
c	2.057 (9)	2.457 (2)	2.064 (7)	2.242 (6) (Me ₂ phen)

^a Legend: a = [PdCl(CH₃)(C₄H₂O₃)(C₁₄H₁₂N₂)] (this work); b = [PtCl(CH₃)(C₂H₄)(6-Mepy-2-CH=N-(S)-CH(Me)(Ph))];^{5a} c = [PtCl(CH(CH₂)₂CH=CH(CH₂)₂CH(OCH₃))(C₁₄H₁₂N₂)];^{5b}

radii, ca. 0.02 Å. However, it should be noted that the differences in M-N and M-C(alkyl) distances conform to the expectations, while the slight elongation of the Pd-Cl distance, 0.035 Å, can be attributed to the observed displacement of the chloride ligand out of the ideal position (Cl-Pd-C(5) angle 174.7 (2)°), determined by the steric pressure of the facing maleic anhydride ligand. Accurate studies on isostructural palladium and platinum complexes²⁴ confirm that a well-defined difference between the atomic radii of these elements does not exist. The longer Pd-C(olefin) distances with respect to the corresponding ones in the platinum complexes is probably related to the poorer donor ability of an olefin carrying electron-withdrawing substituents.²⁴

The maleic anhydride molecule, acting as a unidentate, η² ligand, sits nearly orthogonal to the equatorial plane. It is significantly tilted outward (angle between coordination and ligand planes 114.7°) both as a way to alleviate the contacts with the chlorine ligand (Cl...C(3,4) = 3.3 Å and Cl...O(3) = 3.2 Å) and as a consequence of some rehybridization of the carbon orbitals due to π-back-donation.

Table VI. Bond Distances (Å) in the Coordinated Maleic Anhydride Compared to Those in the Free Molecule²⁴

	C=C	C-C ^a	C=O ^a	C-O ^a
coord	1.410 (7)	1.480 (9)	1.197 (7)	1.392 (7)
free	1.303 (5)	1.470 (5)	1.189 (5)	1.388 (5)

^a Mean value.

Table VII. Out of Aromatic Plane Displacements (Å) of the Equatorial Atoms in Similar Complexes^a

	complex ^b		
	a	b	c
metal	0.38	0.26	0.34
olefinic C	1.01, 0.95	0.68, 0.56	0.82, 0.67

^a The displacements toward the axial methyl ligand are taken to be positive. ^b Legend: a = [PdCl(CH₃)(C₄H₂O₃)(C₁₄H₁₂N₂)] (this work); b = [PtCl(CH(CH₂)₂CH=CH(CH₂)₂CH(OCH₃))(C₁₄H₁₂N₂)];^{5b} c = [Pt(CH₃)(C₂H₄)(C₁₄H₁₂N₂)(NCCCH₃)]BF₄.^{21b}

The latter is confirmed by a significant elongation of the coordinated olefinic bond, compared to the length in the free molecule (1.41 Å against 1.30 Å).²⁵ and by a significant bending away of the hydrogen atoms (average distance from the molecular plane 0.34 Å). The other atoms in the maleic anhydride molecule maintain their normal bond distances (see Table VI) and their planar arrangement upon coordination (maximum deviation from the average plane 0.03 Å).

Concerning the dimethylphenanthroline ligand, whose steric requirements make possible the stable five-coordination, one should note that the aromatic system is not coplanar with the equatorial coordination plane and is slightly tilted toward the methyl ligand (interplanar angle 13.9°). In order to compare the geometry of the present complex with that of analogous platinum species, Table VII shows some atom displacements out of the aromatic ring plane. The values in the palladium complex are consistent with those in the platinum species, and the persistence of this conformational feature in different crystal packings shows its intramolecular origin, very probably residing in the metal-methyl contacts (M...C distances about 3.4 Å in all the compared species). Non-bonded contacts among equatorial atoms show no crowding, with closest distances longer than the van der Waals radii (C(methyl)...C(olefin) = 3.6 Å, H(methyl)...C(olefin) = 3.1 Å, and H(methyl)...H(olefin) = 2.8 Å).

Conclusions

The results we have reported show that a new class of (olefin)palladium(II) complexes, which are five-coordinate, can be obtained by using the same kind of nitrogen bidentate ligands which strongly stabilizes five-coordination in the case of platinum(II) complexes.⁶ The presence of the powerful methyl donor seems to stabilize the five-coordinate species, as suggested by the failure in preparing the analogous dichloro derivative PdCl₂(2,9-Me₂-1,10-phen). A similar trend was also observed for platinum complexes; however, in both cases no equilibrium could be observed between four-coordinate MCl₂(N-N') and five-coordinate MCl₂(N-N')(olefin) species, and no quantitative conclusions can thus be drawn on the relative stabilities of dichloro and chloro methyl complexes. The reason for this effect is not clear. A tentative suggestion, which would require a careful MO treatment to be confirmed or disproved, is a reinforcement of metal to olefin π-back-donation, due to the increased electron density at

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the metal center, caused by the strong donor methyl ligand. Owing probably to the lower strength of the Pd-olefin bond, compared with that of the Pt-olefin bond, a smaller variety of complexes can be prepared, these being limited both in the number of olefins that can bind to the metal and in the number of N-N' ligands giving stable species. At any rate, the influence of steric factors, i.e. the selective stabilization of trigonal-bipyramidal complexes due to the unfavorable steric interactions in the crowded square-planar species **1**, has been confirmed in the case of palladium(II). Qualitative NMR observations have shown that the metal-olefin bond is less labile in the five-coordinate species than it is in the square-planar ones, both toward the exchange with free olefin and toward rotation around the metal-olefin axis. This can be ascribed both to the coordinative saturation of these species, making a binuclear pathway for ligand exchange unfavorable³ (see ref 1, p 246), and to a higher bond rigidity due to an increased contribution of π -back-donation. The latter is particularly relevant in the five-coordinate species we have described, as evidenced by NMR coordination shifts, by the geometrical parameters of **1j**, and by the unprecedented high stability of the complexes with electron-withdrawing olefins.

Experimental Section

¹H NMR spectra were recorded at 60 MHz on a Varian T-60 A spectrometer and at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. CDCl₃ was used as solvent and TMS as internal standard. IR spectra were recorded in Nujol mulls on a Perkin-Elmer 457 spectrophotometer using CsI windows.

Hexane, THF, and diethyl ether were dried over sodium and distilled from sodium benzophenone ketyl under nitrogen before use. Methylene chloride was dried over CaH₂ and distilled before use. N-N' ligands were prepared and stored under nitrogen.

Materials. Ligand **1** is commercially available; II-V were prepared by 1:1 molar ratio condensation of the appropriate aldehyde and primary amine.¹³ The starting palladium complex [PdClMe(SMe₂)]₂ was prepared as previously described,⁹ handled under a nitrogen atmosphere, and stored at -30 °C.

Synthesis of PdClMe(N-N') Complexes 1, 3, 4, and 5. The chloride-bridged dimer **C** was suspended (partially dissolved) in anhydrous diethyl ether (0.01 mmol/mL) at -30 °C under a nitrogen atmosphere. An equimolar amount of the appropriate N-N' ligand, dissolved in diethyl ether (III-V) or in methylene chloride (**1**), was added with stirring, resulting in the formation of a yellow precipitate. The suspension was stirred under a nitrogen atmosphere for 20 min, and the precipitate was collected on a filter and dried, giving the required PdClMe(N-N') complex in 80–90% yield.

Synthesis of PdClMe(N-N')(olefin) Complexes. 1a,b. The four-coordinate complex **1** was dissolved in anhydrous methylene chloride (0.05 mmol/mL) at 0 °C, and the solution was stirred for 10 min under an olefin atmosphere. By addition of anhydrous hexane, the required complex was obtained in about 80% yield as a light yellow solid. **1d-j.** To an anhydrous methylene chloride solution (0.05 mmol/mL) of **1** a large excess of the appropriate olefin was added. By addition of anhydrous diethyl ether, the required complex was obtained in about 70% yield as a light yellow solid. **2a.** To a solution of **C** in anhydrous methylene chloride (0.01 mmol/mL) at -30 °C under a nitrogen atmosphere was added the appropriate N-N' ligand in a 1:1 molar ratio. The product was isolated by evaporating the solvent with a stream of ethylene.

2h. The chloride-bridged dimer **C** was dissolved in anhydrous methylene chloride (0.01 mmol/mL) at -30 °C under a nitrogen atmosphere. The appropriate N-N' ligand was added in a 1:1 molar ratio, and a large excess of the olefin was added to the solution. By addition of anhydrous diethyl ether, the required crude complex was obtained in 60–70% yield.

Synthesis of [PdMe(2,9-Me₂-1,10-phen)(1,5-COD)]BF₄ (1k**[BF₄]).** The four-coordinate complex **1** was dissolved in

Table VIII. Crystal Data and Details of the Structure Determination of [PdClCH₃(C₄H₂O₃)(C₁₄H₁₂N₂)]•C₃H₆O

formula	C ₂₂ H ₂₃ ClN ₂ O ₃ Pd	β , deg	96.79 (3)
<i>M_r</i>	521.28	<i>V</i> , Å ³	2129.7
cryst syst	monoclinic	<i>Z</i>	4
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>d</i> _{calc} , g/cm ³	1.44
<i>a</i> , Å	7.085 (2)	μ (Mo K α), cm ⁻¹	10.0
<i>b</i> , Å	15.880 (2)	<i>F</i> (000)	1032
<i>c</i> , Å	19.062 (3)		
transmission factor range			88–100
scan mode			ω -2 θ
θ range, deg			2.5–22
collected octants			$\pm h, +k, +l$
scan width, deg (+0.35 tan θ)			0.8
prescan speed, deg/min			8
prescan acceptance $\sigma(I)/I$			0.5
maximum scan time, s			120
required counting $\sigma(I)/I$			0.01
decay, %			>50
no. of data collected			1577
no. of data used [<i>I</i> > 2 $\sigma(I)$]			1530
<i>R</i> , <i>R_w</i> , %			2.4, 2.6
<i>k</i> , <i>g</i> ^a			0.7, 9 × 10 ⁻⁴

^a The weighting scheme employed was $w = k/[\sigma^2(F) + |g|F^2]$, where both *k* and *g* were independently determined.

anhydrous methylene chloride (0.01 mmol/mL) at 0 °C under a nitrogen atmosphere. A 10% molar excess of cyclooctadiene was added, followed by an equimolar amount of AgBF₄, dissolved in anhydrous THF (0.05 mmol/mL). After 5 min of stirring, the mixture was filtered through Celite, and the filtrate was concentrated in vacuo. Addition of diethyl ether gave light yellow crystals of the product (**1k**⁺) in about 70% yield.

Determination of the Equilibrium Constants of the Olefin Dissociation Reactions. The equilibrium constants were determined by ¹H NMR analysis (200 MHz) of equilibrium mixtures at 33 °C. This temperature was chosen for consistence with previously reported data on analogous Pt(II) complexes.⁶ The procedure was the same previously described for Pt(II) complexes,⁶ except that the time needed to reach the equilibrium was usually much shorter, ranging from less than 1 min in the case of ethylene and electron-releasing olefins to a few hours in the case of fumarodinitrile. In some cases (see notes to Table II) the equilibrium concentration of the five-coordinate species at room temperature was too low to produce reasonably accurate data, and the equilibrium constant at 33 °C was calculated by extrapolation of three measurements made at lower temperatures (-50 < *T* < 0 °C). Unless otherwise stated, the estimated average error on the dissociation *pK*'s reported in Table II is between 0.1 and 0.2 logarithmic unit.

Structure Determination and Refinement of PdClMe(2,9-Me₂-1,10-phen)(MA) (1j**).** Crystals suitable for X-ray analysis were obtained with the following procedure. To an anhydrous acetone solution of **1** (0.007 mmol/mL) was added an equal volume of a maleic anhydride solution in the same solvent (0.3 mmol/mL). The resulting solution was concentrated to half-volume and kept at room temperature for 48 h, producing pale yellow crystals, which were isolated. An air-sensitive, irregularly shaped crystal with an average diameter of 0.25 mm was selected and sealed under acetone in a glass capillary. The diffraction experiments were carried out at ca. 20 °C on an Enraf-Nonius CAD4 diffractometer. The deterioration of the crystal was tested by detecting at intervals the intensity of three reference reflections and was found to be greater than 50% during the measurements. The structure was solved by conventional methods. The positional parameters of the palladium atom were calculated from the Patterson map. The refinement was carried out by large-block least-squares calculations including the atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms.²⁶ Absorption correction was applied after con-

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vergence of the isotropic refinement according to the method by Walker and Stuart.²⁷ Hydrogen atoms in the aromatic rings were placed in calculated positions (C-H = 1.08 Å) and allowed to ride with respect to their carrier atoms; those in the acetone molecule were omitted. The hydrogen atoms in the methyl groups and in the olefin were picked out from a difference Fourier map and refined with the constraint of fixed C-H distances within 0.01 Å from their average value; the final average value turned out to be 0.9 Å. All the hydrogen atoms were assigned the fixed isotropic temperature factor 0.1 Å². The final difference-Fourier map showed peaks of residual density lower than 0.3 e Å⁻³. Unit cell parameters obtained from least-squares treatment of the orienting reflections along with data collection parameters and numerical details of the structure determination are listed in Table VIII.

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Registry No. 1, 115259-09-1; 1a, 115287-90-6; 1b, 115259-10-4; 1b (diastereomer), 125639-35-2; 1c, 125594-24-3; 1d, 125594-25-4; 1e, 125594-26-5; 1f, 125594-27-6; 1g, 115287-91-7; 1h, 125594-28-7; 1i, 125594-29-8; 1j, 125594-30-1; 1j-(CH₃)₂CO, 125760-56-7; 1k⁺, 125610-36-8; 2a, 125594-31-2; 2h, 125594-32-3; 3, 125594-33-4; 3a, 125594-34-5; 3i, 125594-35-6; 3i (diastereomer), 125760-56-7; 4, 125594-36-7; 4a', 125594-37-8; 4a'', 125639-37-4; 5, 125594-38-9; [PdClMe(Me₂S)]₂, 101308-24-1; 6-Mepy-2-CH=NC₆H₄OMe, 26825-36-5.

Supplementary Material Available: Tables of fractional atomic coordinates for the hydrogen atoms, anisotropic thermal parameters, and analytical data (3 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Fluoroorganometallic Chemistry: Decarbonylation of Cyclic Perfluoroacyl Complexes

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The tetracarbonylferrate dianion reacts with perfluorodiacyl chlorides to yield perfluorometallacycloalkanediones. For instance, perfluorosuccinyl and perfluoroglutaryl chlorides yield $\text{Fe}(\text{CO})_4(\text{COCF}_2\text{CF}_2\text{CO})$ and $\text{Fe}(\text{CO})_4(\text{COCF}_2\text{CF}_2\text{CF}_2\text{CO})$, respectively. Extrusion of one CO from the six-membered ring of $\text{Fe}(\text{CO})_4(\text{COCF}_2\text{CF}_2\text{CF}_2\text{CO})$ yields the perfluoro-1-metallacyclopentan-2-one $\text{Fe}(\text{CO})_4(\text{CF}_2\text{CF}_2\text{CF}_2\text{CO})$, and extrusion of the second CO yields the perfluorometallacyclobutane $\text{Fe}(\text{CO})_4(\text{CF}_2\text{CF}_2\text{CF}_2)$. In the perfluorosuccinyl chloride derived system, the four-membered monoacyl is not observed, because the second extrusion of CO proceeds quickly to give a three-membered ring. There has been no evidence of the reverse reaction, insertion of CO into a metal-fluoroalkyl bond, including that of $\text{Fe}(\text{CO})_4(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2)$. Four of the fluorometallacycle complexes in this series have been characterized crystallographically. $\text{Fe}(\text{CO})_4(\text{COCF}_2\text{CF}_2\text{CO})$ crystallizes in the space group *C2/c* with cell dimensions $a = 10.957$ (2) Å, $b = 8.652$ (1) Å, $c = 12.335$ (2) Å, and $\beta = 118.68$ (1)°. $\text{Fe}(\text{CO})_4(\text{COCF}_2\text{CF}_2\text{CF}_2\text{CO})$ crystallizes in the space group *P2₁/c* with cell dimensions $a = 11.433$ (1) Å, $b = 9.372$ (1) Å, $c = 12.817$ (1) Å, and $\beta = 116.11$ (1)°. $\text{Fe}(\text{CO})_4(\text{CF}_2\text{CF}_2\text{CF}_2\text{CO})$ crystallizes in the space group *P2₁/c* with cell dimensions $a = 7.079$ (1) Å, $b = 13.084$ (2) Å, $c = 11.887$ (1) Å, and $\beta = 101.34$ (1)°. $\text{Fe}(\text{CO})_4(\text{CF}_2\text{CF}_2\text{CF}_2)$ crystallizes in the space group *Pnma* with cell dimensions $a = 15.161$ (2) Å, $b = 9.222$ (1) Å, and $c = 7.229$ (1) Å.

Introduction

As part of our ongoing investigation¹ of the role of organometallic chemistry in the synthesis of organofluorine compounds, we have investigated the carbonylation and decarbonylation reactions of metal-fluoroalkyl bonds. Early work in fluoroorganometallic chemistry concerned the oxidative coupling of tetrafluoroethylene by low-valent transition-metal complexes to form perfluorometalla-

cyclopentane compounds.^{2,3} The clean formation of a $-\text{C}_4\text{F}_8-$ fragment from relatively inexpensive starting ma-

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