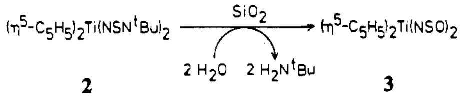
5 and **6** is confirmed by comparison of the IR spectra with those of both $(Ph_3P)_2Rh(CO)(NSO)$[18] and of K[NSO].[31]



$$(\eta^5\text{-}C_5H_5)_2Ti(NSN^tBu)_2 \xrightarrow[2\,H_2O \;\; 2\,H_2N^tBu]{SiO_2} (\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$$

2 **3**

According to the ^1H and ^{13}C NMR spectra the ring systems in **5** and **6** are equivalent: For **5** only one signal is observed in both the ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of the methyl-substituted derivative **6** contains a singlet for the methyl protons and a singletlike multiplet for the four remaining ring protons; in the ^{13}C NMR spectrum of **6** a signal for the methyl group and three signals for the different kinds of ring carbon nuclei are observed. The spectra are independent of temperature; therefore, the NMR data suggest either rotation of the two ring systems or the existence of symmetrical rotamers. However, the NMR spectra are not conclusive as to the *E* or *Z* configuration of the NSO moiety, and therefore a X-ray crystallographic structure determination of **5** was carried out. Since no isomerization is observed by NMR spectroscopy, the configuration of **5** and **6** in solution is likely to be the same (*Z*,*Z*) as found for **5** in the solid state.

Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$ (5). Figure 2 shows an ORTEP drawing of a molecule of **5**; bond distances and angles are listed in Table III. They are not corrected for the effects of thermal motion. The scatter in the bond distances for the C_5 ring (1.340 (9)–1.386 (12) Å) reflects its pronounced libration motion. The molecule has crystallographic C_2 symmetry. The atoms of the $Ti(NSO)_2$ moiety are nearly coplanar (deviations (Å) from the N–Ti–N′ plane: S, 0.03; O, 0.02). The centroids of the C_5 rings and the coordinated N atoms define a distorted tetrahedron. The coordination geometry about the titanium atom is very similar to that of many other $(\eta^5\text{-}C_5H_5)_2TiX_2$ complexes. In Table IV $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$ (**5**) is compared in particular with other $(\eta^5\text{-}C_5H_5)_2Ti^{IV}$ compounds that contain monodentate ligands bonded via nitrogen atoms. The relatively large Ti–N–S bond angle of 150.8 (3)° in **5** is consistent with the assumption that the Ti–N bond has some double bond character; an extreme formulation for this situation would be Ti=N=S=O.

The view that the titanium atom tends to achieve an effective 18-electron configuration by ligand π-donation has been suggested by Huffman et al. for Ti–Cl and Ti–OR bonds in titanocene derivatives.[32] Judging from the Ti–N bond distances, all complexes listed in Table IV have nearly the same degree of Ti–N π-bonding.

The geometry of the NSO group in **5** agrees within reasonable limits with the geometry of the NSO group in $(Ph_3P)_2Rh(CO)(NSO)$,[18] the values for *d*(N–S), *d*(S–O), and ∠(N–S–O) in the Rh complex being 1.480 (12) Å, 1.509 (10) Å, and 122.5 (5)°. There are no abnormally short intermolecular contacts between individual molecules. Contacts (Å) less than 3.5 Å are as follows: O···S (at $^1/_4 - x$, $^1/_4 + y$, $^1/_4 + z$), 3.44 (1); O···C(2) (at $^1/_4 - x$, $^1/_4 + y$, $^1/_4 + z$), 3.31 (1).

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: ^1H NMR spectra of **2** at −60, −26, and +25 °C (Figure 1) and a complete list of atomic parameters (anisotropic thermal parameters for non-hydrogen atoms and *x*, *y*, *z* values for hydrogen atoms) (2 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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(31) Armitage, D. A.; Brand, J. C. *J. Chem. Soc., Chem. Commun.* **1979**, 1078.

(32) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

(33) Anderson, S. J.; Brown, D. S.; Norbury, M. M. *J. Chem. Soc., Chem. Commun.* **1974**, 996.

(34) Chiesi-Villa, A.; Manfredotti, A. G.; Guastini, C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 909.

(35) De Gill, E. R.; De Burguera, M.; Rivera, A. V.; Maxfield, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 578.

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Complexes of Binucleating Ligands. 20. Complexes of a New, Easily Accessible Binucleating Ligand Containing an Aliphatic Thiolate Bridging Center

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2-(Acetylthio)-*N*,*N*′-bis(pyridin-2-ylmethyl)butanediamide (V) is very simple to synthesize and acts as a convenient precursor to a new type of thiolate-based binucleating ligand, hereafter L^{3-}, represented in the generalized binuclear complex III. Reaction of V with $M(CH_3CO_2)_2$ (M = Pd(II), Ni(II), Cu(II)) leads to rapid metal-promoted S-deprotection and yields $LM_2(\mu\text{-}CH_3CO_2)$ simply and cleanly. $LCu_2(CH_3CO_2)$, a rare example of a dicopper(II) complex with a bridging thiolate center, shows very weak magnetic exchange between the cupric centers. Several diamagnetic Pd^{II}_2 complexes (and some related Ni^{II}_2 complexes) were obtained by substitution of the bridging acetate in the appropriate $LM_2(CH_3CO_2)$ by other carboxylates, pyrazolates, I^-, N_3^-, SCN^-, $RCONH^-$ (the conjugate base of a carboxamide), and $(CH_3)_2NO^-$ (the conjugate base of *N*,*N*-dimethylhydroxylamine) and were studied by ^1H and ^{13}C NMR spectroscopy. Reaction of $LPd_2(CH_3CO_2)$ with NaI gives $(LPd_2I_2)Na$ and with NaN_3 gives $(LPd_2(N_3)_2)Na$, but reaction with NaSCN gives $LPd_2(SCN)$. The relative sluggishness of reaction between $LPd_2(RCO_2)$ and carboxamides, $R'CONH_2$, to give $LPd_2(R'CONH)$ suggests a sterically more congested bridging site in LPd_2^+ than in closely related earlier systems. Because of the asymmetry of L^{3-} geometrical isomeric forms of $LPd_2(R'CONH)$ are possible (VI and VII) and are observed by NMR spectroscopy. Reaction of $LPd_2(CH_3CO_2)$ with *N*,*N*-dimethylhydroxylamine and base gives $LPd_2((CH_3)_2NO)$, which exists in only one of the two possible geometrical isomeric forms and which shows nonequivalent *N*-methyl groups.

Introduction

Complexes of binucleating ligands may provide new sorts of chemistry occurring under the simultaneous influence of two metal centers. Binucleating ligands constructed around a central hinging thiolate center show particular promise in this area for the reasons outlined below. Studies of complexes of the type I[1] and related systems[2] have revealed that the site occupied by Z can accommodate three-atom bridges (e.g. $\mu\text{-}RCO_2^-$), two-atom bridges (e.g.

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(1) Louey, M.; Nichols, P. D.; Robson, R. *Inorg. Chim. Acta* **1980**, *47*, 87.

(2) (a) Hughes, J. G.; Robson, R. *Inorg. Chim. Acta* **1979**, *35*, 87. (b) Krautil, P.; Robson, R. *J. Coord. Chem.* **1980**, *10*, 7.

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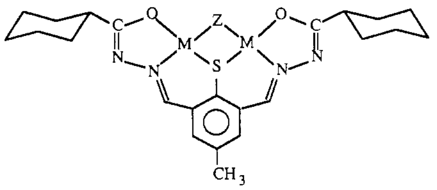
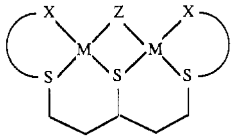


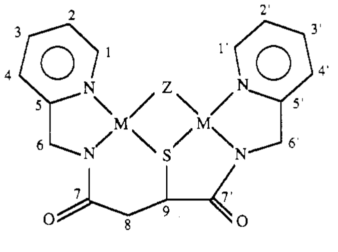
I

μ-pyrazolato), or one-atom bridges provided they are large enough (e.g. μ-I^-). In addition, the hinging sulfur atom provides enough flexibility and allows sufficient extension of the metal-metal separation for two separate, unlinked monodentate ligands to be bound, one to each metal at the site occupied by Z in I.[3] An example of a condensation, occurring at the dipalladium(II) site of a complex derived from the ligand in I, was reported recently,[4] namely, nucleophilic attack by a hydroxide ion bound to one palladium center upon a nitrile activated by coordination to an adjacent palladium, thereby generating a carboxamido bridge. We have recently extended this bridging site chemistry to provide binuclear catalysts capable of promoting the hydration of several thousand moles of nitrile to amide per mole of complex.[5] This first example provides encouragement that other processes promoted by metal pairs are waiting to be discovered. In the present paper we describe the synthesis and some basic coordination chemistry of a new binucleating ligand that provides the most effective binuclear catalyst for nitrile hydration we thus far have available. The ligand also provides complexes capable of catalyzing the hydration of acrylonitrile specifically to acrylamide.[5]

Existing approaches to complexes of binucleating ligands containing a bridging thiolate center, whether aromatic as in I[1,2] or aliphatic as in II,[6] are time-consuming and tedious. This constitutes a significant barrier to more rapid exploitation of these systems. We report here a new and simple approach to ligands with a hinging aliphatic thiolate center. The work described is concerned with the particular binucleating ligand (hereafter L^{3-}) represented in the complex III, formulated LM_2Z, but the synthetic approach appears, in principle, to be of more general applicability.



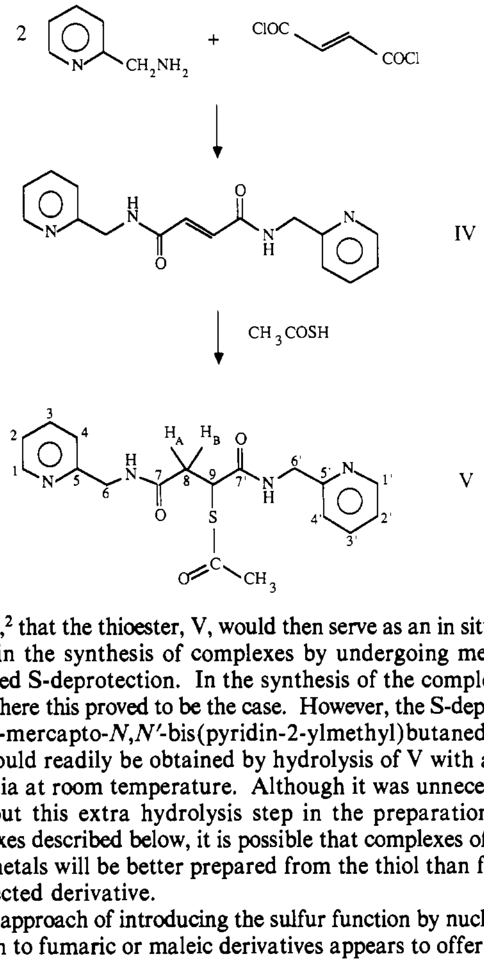
II



III

Results and Discussion

Scheme I



The Ligand. The ligand synthesis is outlined in Scheme I. The synthetic strategy was to introduce the sulfur function as a thioester group by nucleophilic addition across a central fumaric diamide unit, IV → V, in the hope, based on earlier experience with related systems,[2] that the thioester, V, would then serve as an in situ source of L^{3-} in the synthesis of complexes by undergoing metal-ion-promoted S-deprotection. In the synthesis of the complexes described here this proved to be the case. However, the S-deprotected thiol 2-mercapto-*N*,*N'*-bis(pyridin-2-ylmethyl)butanediamide, LH_3, could readily be obtained by hydrolysis of V with aqueous ammonia at room temperature. Although it was unnecessary to carry out this extra hydrolysis step in the preparation of the complexes described below, it is possible that complexes of certain other metals will be better prepared from the thiol than from the S-protected derivative.

This approach of introducing the sulfur function by nucleophilic addition to fumaric or maleic derivatives appears to offer general access to related binucleating ligands with a variety of terminal donor groups.

The addition of thioacetic acid across the fumaric double bond generates a chiral carbon center (C9 in V), and consequently the two protons of the adjacent methylene group become intrinsically nonequivalent[7] ($H8_A$ and $H8_B$ in V). This nonequivalence is apparent in the ^1H NMR spectrum of V, in which $H8_A$ and $H8_B$ appear as a multiplet closely approximating to a doublet of quartets centered at 2.92 ppm, the doubling arising from coupling to the single adjacent methine proton H9. The latter gives rise to a multiplet largely obscured by two apparent "singlets" at 4.51 and 4.57 ppm arising from the methylene groups adjacent to pyridine, namely H6 and H6' in V. The two protons within each of these 6- and 6'-methylene groups are also in principle intrinsically nonequivalent, and although this nonequivalence is not apparent in the ^1H NMR spectrum of the S-protected ligand, it is clearly seen in the spectra of the metal complexes, discussed below, and also in the spectrum of LH_3. In the latter case the chemical shift difference between the two protons within a particular CH_2 was so small that the complete quartet structure could not be discerned and coupling constants could not be determined; nevertheless, the intrinsic nonequivalence was unmistakable, one methylene appearing as a pair of components at 4.59 and 4.57 ppm and the other as a pair at 4.53 and 4.52 ppm. H9 of LH_3 (numbering as for V) appears separated from the H6,6' signals as an ill-defined multiplet centered at approximately 3.87 ppm, coupled to $H8_A$ and $H8_B$ and also to the SH proton, which, in turn, appears as a broadened doublet at approximately 2.48 ppm. On D_2O exchange the SH signal disappears and the H9 signal sharpens to a multiplet closely resembling a triplet centered at 3.87 ppm, the coupling to the H8 protons being retained.

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(3) Crossley, T. E.; Hoskins, B. F.; McDonald, I. A. S.; Robson, R. *Inorg. Chim. Acta* **1986**, *111*, 99.

(4) Louey, M.; McKenzie, C. J.; Robson, R. *Inorg. Chim. Acta* **1986**, *111*, 107.

(5) Part 21 of Complexes of Binucleating Ligands: McKenzie, C. J.; Robson, R., submitted for publication.

(6) Kelson, R.; Robson, R. *J. Coord. Chem.* **1979**, *9*, 235.

(7) Jackman, L. M.; Sternell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon: Oxford, England, 1969; p 373ff.

Table I. NMR Features Originating in L

	^{1}H NMR, ppm				^{13}C NMR, ppm								
	H_A	H_B	J_{AB}, Hz	solvent	1,1′	2,2′,4,4′	3,3′	5,5′	6,6′	7,7′	8	9	solvent
S-protected ligand, V	4.51	4.51	...	*a*	149.0	122.2, 121.8	136.7	156.9	45.0	170.5	42.4	37.0	*a*
	4.57	4.57	...			121.3			44.7	169.8			
LH_3	4.59	4.57	...	*a*	150.0	122.2	136.6	156.6	45.1	171.8	42.4	39.0	*a*
	4.53	4.52	...		149.1	121.9			44.6	170.0			
						121.7							
$LPd_2(CH_3CO_2)$	5.03	5.03	...	*a*									
	5.15	4.61	21.2										
$LNi_2(CH_3CO_2)$	4.75	4.57	20.9	*a*									
	4.53	4.34	21.5										
$LPd_2(CH_3CH_2CO_2)$	5.02	5.02	...	*a*	145.8	122.6, 122.1,	138.6[c]	166.9	60.5	184.2	45.9	43.1	*a*
	5.19	4.69	20.3		145.0	121.2, 120.9		165.0	55.9	180.1			
$LPd_2((CH_3)_3CCO_2)$	5.03	5.03	...	*a*	145.0	122.0, 121.6,	137.88	166.2	60.2	187.9	45.3	42.9	*a*
	5.00	4.76	20.6		144.3	121.5, 121.4	137.91	164.3	55.7	179.2			
$LNi_2((CH_3)_3CCO_2)$	4.82	4.56	20.0	*a*	145.2	122.2, 121.6,	138.4	166.2	58.9	180.8	41.5	38.8	*a*
	4.52	4.34	20.7		144.5	120.5, 120.1	137.7	165.8	54.3	179.6			
$LPd_2(CF_3CO_2)$	5.18	4.88	19.2	*a*									
	4.96	4.78	20.0										
$LPd_2(C_3H_3N_2)$[e]	5.57	4.59	18.6	*a*	147.7	123.6[c]	140.0, 139.6,	166.6	57.3	178.9	49.7	45.3	*b*
	5.04	4.70	22.3		147.5	122.7, 121.6	139.4, 139.2[d]	164.7	54.9	170.2			
$LNi_2(C_3H_3N_2)$	4.46	4.46	...	*a*	148.1	122.7, 122.4,	142.7, 142.3,	166.6	55.9	180.9	47.9	44.0	*a*
	4.72	4.06	18.8		147.2	121.9, 121.8	138.5, 138.4[d]	165.8	54.1	173.2			
$LPd_2((CH_3)_2C_3HN_2)$[f]	5.23	4.86	19.8	*a*	149.0	122.5, 122.2,	138.6	167.7	59.4	180.0	47.0	45.6	*a*
	5.05	4.71	20.5		148.5	121.2[c]	138.5	165.8	55.4	171.1			
$(LPd_2(N_3)_2)Na$	4.65	4.65	...	*b*	146.2	123.0, 122.7	138.8[c]	166.5	58.3	178.4	45.1	43.1	*b*
	5.22	4.32	20.5		146.1	123.3, 121.1		165.0	54.1	170.2			
$(LPd_2I_2)Na$	4.95	4.53	19.0	*b*									
	5.47	4.31	20.0										
$LPd_2(CH_3CONH)$	complex			*a*									
$LPd_2(C_6H_{11}CONH)$[g]	complex			*a*	146.2,	122.5, 122.3	138.3[c]	168.4	60.5	185.5	47.6	45.2	*a*
					145.8	121.8, 121.5,		167.0	60.0	184.6			
					145.2	120.7		166.4	55.7	180.2			
					144.7			165.2	55.4	179.4			
$LPd_2(CH_2CHCONH)$[h]	complex			*a*	147.4	124.7, 123.3 + sh	139.2[c]	167.3	60.5	179.0	42.3	41.8	*b*
					147.3	122.8, 121.6 + sh		166.3	59.9	178.0	42.6		
					145.1			165.0	55.2	173.6			
					143.8			164.2	55.1	172.4			
$LP_2((CH_3)_2NO)$[i]	5.07	4.81	19.6	*a*	146.4	123.2, 122.8	138.6	168.1	59.1[j]	180.8	46.7	42.9	*a*
	5.02	4.66	21.0		145.5	122.0, 121.0	138.3	165.1	58.6	171.2			
									56.8				
									55.4				

[a] $CDCl_3$. [b] $(CD_3)_2SO$. [c] Peak heights consistent with two superimposed resonances. [d] Four peaks arise from C3 + C3′ of L^{3-} together with α-C + α'-C of pyrazolate, but specific assignments cannot be made. [e] $C_3H_3N_2^-$ = conjugate base of pyrazole. [f] $(CH_3)_2C_3HN_2^-$ = conjugate base of 3,5-dimethylpyrazole. [g] $C_6H_{11}CONH^-$ = conjugate base of cyclohexanecarboxamide. [h] $CH_2CHCONH^-$ = conjugate base of acrylamide. [i] $(CH_3)_2NO^-$ = conjugate base of *N*,*N*-dimethylhydroxylamine. [j] Four peaks arise from C6 + C6′ of L^{3-} together with CH_3–N + CH_3'–N of $(CH_3)_2N$–O bridge.

^{13}C NMR spectra of the S-protected ligand and LH_3 were entirely consistent with the intended structures; data for C1–C9 are listed in Table I, and the two outstanding thioester carbon resonances of the S-protected ligand not included in Table I appeared at 30.3 ppm (CH_3) and 195.1 ppm (C=O).

Complexes. General Features of NMR Spectra of Complexes. The features arising from L^{3-} in the ^{1}H NMR spectra of the Pd(II) and Ni(II) complexes described below were complex but explicable in general terms and consistent with the binuclear arrangements of the type III. Pyridine resonances were second order and generally uninformative. The chemical shift of H9 (see structure III) moved much closer in the spectra of the complexes to those of $H8_A$ and $H8_B$ than in the spectra of LH_3 and the S-protected ligand, resulting in complex ABC patterns in the region 2.5–3.6 ppm. The two nonidentical methylene groups, 6 and 6′, generally appeared in an otherwise clear region of the spectrum, 3.9–5.6 ppm, and constituted the most useful L-derived features. As discussed above, the two protons within each methylene group are intrinsically nonequivalent and the two methylene groups together give rise to either two interpenetrating but generally well-resolved AB quartets or one AB quartet and one "singlet" (the latter arising from the two protons within one methylene group accidentally having very similar chemical shifts). Chemical shifts of $H6_A$, $H6_B$, and $H6'_A$, $H6'_B$ together with coupling constants (where discernible) are given in Table I. Features arising from bridging species were generally easily identifiable and assignable and are presented in Table II.

In the ^{13}C NMR spectra, which were generally consistent with the anticipated bridged arrangements, all the carbon atoms could be satisfactorily accounted for. ^{13}C NMR features originating in L^{3-} are given in Table I and those arising in the bridging species in Table II.

Carboxylate-Bridged Complexes. The metal-ion-promoted S-deprotection of V by Pd(II), Ni(II), or Cu(II) was facile and clean; only a few minutes' reaction of V with the metal acetate in either boiling chloroform (for Pd(II)) or boiling methanol (for Ni(II) and Cu(II)) was required to generate $LM_2(CH_3CO_2)$.

Bands in the IR spectrum of the S-protected ligand V at 3280 and 3330 cm^{-1} due to amide ν_{NH} and at 1705 cm^{-1} due to the thioester ν_{CO} disappeared in the IR spectra of these three acetate complexes, which were very similar to each other. In all three cases the strongest band in the spectrum was the amide I band, primarily ν_{CO}, which was lowered from 1640 cm^{-1} in the S-protected ligand to 1605 cm^{-1} in $LPd_2(CH_3CO_2)$, 1610 cm^{-1}, in $LNi_2(CH_3CO_2)$, and 1600 cm^{-1} in $LCu_2(CH_3CO_2)$ as is consistent with the deprotonation of the amide group.[8] These and other complexes of L^{3-} readily absorbed water from the atmosphere, as indicated by microanalytical data and also by bands at ca. 3400 cm^{-1} in the IR spectra. Several strong L-derived bands were apparent in the range 1400–1600 cm^{-1}, making definite assignment of the bridging carboxylate bands difficult, but comparison with

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(8) (a) Chapman, R. L.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1981**, *52*, 161. (b) Nonoyama, M. *Inorg. Chim. Acta* **1975**, *13*, 5.

Table II. NMR Features Originating in the Exogenous Bridge

	^{13}C NMR, ppm	solvent	^{1}H NMR, ppm[j]
$LPd_2(CH_3CO_2)$			2.17 (s) [CH_3]
$LNi_2(CH_3CO_2)$			1.85 (s) [CH_3]
$LPd_2(CH_3CH_2CO_2)$	10.6 (CH_3); 30.7 (CH_2); 171.0 (OCO)	*a*	1.16 (t) [CH_3]; 2.43 (q) [CH_2]
$LPd_2((CH_3)_3CCO_2)$	28.2 (CH_3); 40.3 (>C–); 170.2 (OCO)	*a*	1.23 (s) [CH_3]
$LNi_2((CH_3)_3CCO_2)$	27.7 (CH_3); 49.2 (>C–); 147.9 (OCO)	*a*	1.00 (s) [CH_3]
$LPd_2(C_3H_3N_2)$[c]	105.7 (β-C); 2 of 140.0, 139.6, 139.4, 139.2[d] (α-C, α'-C)	*b*	6.29 (t) [β-H]; 7.88 (d), 7.49 (d) [α-H, α'-H]
$LNi_2(C_3H_3N_2)$	107.6 (β-C); 2 of 142.7, 142.3, 138.5, 138.4[d] (α-C, α'-C)	*a*	6.12 (t) [β-H]; 7.30 (d), 7.05 (d) [α-H, α'-H]
$LPd_2((CH_3)_2C_3HN_2)$[e]	105.5 (β-C); 149.9, 149.6 (α-C,α'-C); 13.8, 13.6 (α-CH_3, α'-CH_3)	*a*	2.16, 2.33 [α-CH_3, α'-CH_3]; 5.85 (s) [β-H]
$LPd_2(CH_3CONH)$			2.16 (s) [CH_3]
$LPd_2(C_6H_{11}CONH)$[f]	170.9 (amide C); 44.0, 43.3 (C_a, 2 isomers); 25.9 (C_c, $C_{c'}$, C_d); 31.0 (C_b, $C_{b'}$)	*a*	cyclohexyl H's, broad
$LPd_2(CH_2CHCONH)$[g]	169.0 (amide C); 132.1, 132.4 (CH, 2 isomers)	*b*	complex, 5.5–6.3 [CH_2CH–]
$LPd_2((CH_3)_2NO)$[h]	2 of 59.1, 58.6, 56.8, 55.4 (CH_3–N and CH_3'–N)[i]	*a*	3.17 (s) [CH_3–N]; 3.05 (s) [CH_3'–N]

[a] $CDCl_3$. [b] $(CD_3)_2SO$. [c] $C_3H_3N_2^-$ = conjugate base of pyrazole. [d] Four peaks arise from C3 + C3′ of L^{3-} together with α-C + α'-C of pyrazolate, but specific assignments cannot be made. [e] $(CH_3)_2C_3HN_2^-$ = conjugate base of 3,5-dimethylpyrazole. [f] $C_6H_{11}CONH^-$ = conjugate base of cyclohexanecarboxamide. See structure VIII for identification of carbons. [g] $CH_2CHCONH^-$ = conjugate base of acrylamide. [h] $(CH_3)_2NO^-$ = conjugate base of *N*,*N*-dimethylhydroxylamine. [i] Four peaks arise from C6 + C6′ of L^{3-} together with CH_3–N + CH_3'–N of $(CH_3)_2N$–O^- bridge. [j] The solvent in all cases is $CDCl_3$.

the spectra of other complexes of L^{3-} leads to the following assignments: ν_{OCO}(sym) 1400 cm^{-1} in all three acetates; ν_{OCO}(asym) 1545 cm^{-1} ($LPd_2(CH_3CO_2)$), 1540 cm^{-1} ($LNi_2(CH_3CO_2)$), and 1540 cm^{-1} ($LCu_2(CH_3CO_2)$). These are in good agreement with carboxylate band frequencies observed in other acetate-bridged complexes.[1,2,9]

^{1}H NMR data for $LPd_2(CH_3CO_2)$ and $LNi_2(CH_3CO_2)$ are presented in Tables I and II. The acetate-bridged complexes were too insoluble to allow ^{13}C NMR spectra to be recorded. Complexes in which the acetate bridge had been replaced by propionate, pivalate, or trifluoroacetate were therefore isolated in the hope of obtaining derivatives sufficiently soluble to provide not only good quality ^{13}C NMR data but also more easily recrystallizable materials with a view to growing crystals suitable for X-ray crystallography. All attempts to grow satisfactory crystals have thus far failed; on the rare occasions when single crystals could be obtained, they proved to be significantly disordered.[10] $LPd_2(CH_3CH_2CO_2)$, $LPd_2((CH_3)_3CCO_2)$, and $LNi_2((CH_3)_3CCO_2)$ did prove sufficiently soluble to provide ^{13}C NMR spectra in which all carbons could be accounted for; in these ^{13}C spectra and in all the carboxylate ^{1}H spectra (Tables I and II) features arising from the bridging carboxylate were readily identified. All the evidence supports the general conclusion that the carboxylate anion can be incorporated in both LPd_2^+ and LNi_2^+ in the three-atom bridging mode, which has been demonstrated unambiguously by X-ray crystallography in carboxylate-bridged complexes of the related binucleating ligand represented in I.[11]

The close similarity between the IR spectra of $LCu_2(CH_3CO_2)$, $LNi_2(CH_3CO_2)$, and $LPd_2(CH_3CO_2)$ points to a common basic molecular structure. Many studies have been concerned with the dependence of magnetic exchange within binuclear copper(II) complexes upon the nature of the bridging species.[12] In this context the way in which a thiolate sulfur center might mediate in the exchange would be of considerable interest. However, very few thiolate-bridged dicopper(II) complexes are known. To our knowledge, magnetic studies have been reported on only three such complexes, all derived from the thiophenoxide-based binucleating ligand in I or closely related systems and all having the pyrazolate anion as the exogenous bridge.[2b,13] Zero or very weak (ferromagntic) exchange was observed in these cases, in marked contrast to the very strong antiferromagnetic interaction observed in similar complexes with the thiophenoxide sulfur bridge replaced by a phenoxide oxygen. $LCu_2(CH_3CO_2)$ differs from these earlier examples in that the thiolate bridge is aliphatic rather than aromatic and the exogenous bridge is a three-atom-bridging acetate rather than a two-atom-bridging pyrazolate, but the magnetic properties appear very similar. The magnetic moment increases from 1.90 μ_B per copper at 283 K to 2.06 μ_B at 93 K, and Curie–Weiss behavior is observed down to liquid-nitrogen temperature with a positive Weiss constant of 17 K possibly indicative of weak ferromagnetic interaction.

Pyrazolates. The ability of the LPd_2^+ and LNi_2^+ units to incorporate two-atom bridges was demonstrated by the replacement of bridging acetate by bridging pyrazolate ion, simply by heating the acetate complex in solution with pyrazole. A related complex of 3,5-dimethylpyrazole, $LPd_2((CH_3)_2C_3HN_2)$, was likewise isolated, where $(CH_3)_2C_3HN_2^-$ represents the conjugate base of 3,5-dimethylpyrazole. The ^{1}H and ^{13}C NMR spectra of these three complexes (Tables I and II) were entirely consistent with the proposed binuclear arrangements with two-atom, N,N′-bridging pyrazolate units. Nonequivalence of the groups adjacent to the pyrazole nitrogens, arising from the asymmetry of L^{3-}, was apparent in both the ^{1}H and ^{13}C NMR spectra; thus, in the two complexes of unsubstituted pyrazole two different carbons α to nitrogen and two different α-hydrogens were observed, while in the dimethylpyrazole complex two different ring carbons α to nitrogen were apparent in the ^{13}C spectrum and two different methyls were apparent in both the ^{13}C and ^{1}H NMR spectra.

Iodide, Azide, and Thiocyanate Derivatives. Reaction of $LPd_2(CH_3CO_2)$ with an excess of either sodium azide or sodium iodide gave products that proved to be the sodium salts of the complex anions $LPd_2(N_3)_2^-$ and $LPd_2I_2^-$, rather than the anticipated neutral $LPd_2(N_3)$ and LPd_2I. Reaction of $LPd_2(CH_3CO_2)$ with equivalent amounts of sodium azide or sodium iodide gave unchanged acetate complex together with the diazido and diiodo anionic complexes, indicating these binuclear anions have considerable stability compared with that of the neutral $LPd_2(N_3)$ and LPd_2I. Both $(LPd_2(N_3)_2)Na$ and $(LPd_2I_2)Na$ were insoluble in chloroform and only marginally soluble in dimethyl sulfoxide, in which solvent NMR spectra were recorded, although the solubility of the iodo complex was too low to afford a ^{13}C spectrum. The NMR data for these two complexes given in Table I indicate a single LPd_2-derived complex species in both cases but throw no light on the nature of the azido and iodo binding.

Thiocyanate ion, in contrast to the case for azide and iodide, reacts with $LPd_2(CH_3CO_2)$ in the anticipated manner to yield $LPd_2(SCN)$. The marked insolubility of this complex precluded NMR observations and perhaps points to a polymeric structure involving thiocyanate bridging between, rather than within, LPd_2^+ units. The IR spectrum of $LPd_2(SCN)$ shows two sharp, well-

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(9) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(10) Hoskins, B. F.; McDonald, I. A. S., unpublished results.

(11) Hoskins, B. F.; McDonald, I. A. S. *Aust. J. Chem.* **1984**, *37*, 725.

(12) (a) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107. (b) Kahn, O. *Inorg. Chim. Acta* **1982**, *62*, 3. (c) Murray, K. S. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1986; Vol. II, p 161. (d) Mazurek, W.; Kennedy, B. J.; Murray, K. S.; O'Connor, M. J.; Snow, M. R.; Rogers, J. R.; Wedd, A. G.; Zwack, P. R. *Inorg. Chem.* **1985**, *24*, 3258.

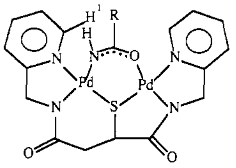
(13) Iliopoulos, P.; Murray, K. S.; Robson, R.; Wilson, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.*, in press.

resolved bands at 2110 and 2160 cm^{-1} but is otherwise very similar to those of $(LPd_2I_2)Na$ and $(LPd_2(N_3)_2)Na$ and affords no useful structural clues.

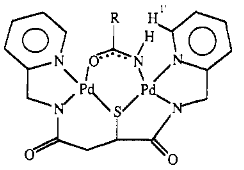
Complexes with Conjugate Bases of Carboxamides at the Bridging Site. An extensive range of bridge substitutions with dipalladium(II) complexes of the type I has been reported, one example of which was the ready replacement of bridging acetate in a complex we shall represent as $L'Pd_2(CH_3CO_2)$, by bridging deprotonated amide.[1] When $L'Pd_2(CH_3CO_2)$ was merely heated with the neutral amide, the reaction

$$L'Pd_2(CH_3CO_2) + RCONH_2 \rightleftharpoons L'Pd_2(RCONH) + CH_3COOH$$

appeared to go essentially to completion. Even though the neutral amide is a very much weaker acid than acetic acid, it appears that the affinity of the $L'Pd_2^+$ system is so much greater for $RCONH^-$ than for $CH_3CO_2^-$ that essentially complete reaction occurs. Attempts to repeat this sort of bridge substitution with the presently described $LPd_2(RCO_2)$ derivatives revealed markedly different behavior; reaction was much more sluggish and proceded only as far as an equilibrium mixture in which a considerable fraction of the initial carboxylate complex remained unchanged. The relative reluctance of the LPd_2^+ system, compared with the case for $L'Pd_2^+$, to accept at the bridging site the conjugate base of the amide has important implications with regard to the binuclear catalysis of nitrile hydration to be described in a future report.[5] This reluctance probably stems from the unfavorable steric clash between the NH of the bridging group and the closely adjacent H1 or H1′ of L^{3-} as in the two possible geometrical isomers VI and VII. For preparative purposes, the equilibrium described above could readily be displaced to provide amido-bridged complex free of carboxylate complex simply by adding the base 1,8-diazabicyclo[5.4.0]-7-undecene (dbu). The first amide-derived complex to be isolated in this way was $LPd_2(CH_3CONH)$, which proved to be insufficiently soluble to provide complete ^{13}C NMR data, although the ^1H NMR spectrum was observable (Tables I and II). $LPd_2(C_6H_{11}CONH)$ (where C_6H_{11} = cyclohexyl) was therefore prepared, in the hope that the cyclohexyl group would improve the solubility, and both ^1H and ^{13}C NMR spectra proved to be observable in this case. In our investigations of binuclear catalyzed hydration of nitriles[5] (to be described separately) we have concentrated upon acetonitrile and acrylonitrile; NMR characterization of complexes with acetamide- and acrylamide-derived bridges was therefore important, and for this reason we also isolated $LPd_2(CH_2CHCONH)$ (where $CH_2CHCONH^-$ represents the conjugate base of acrylamide).

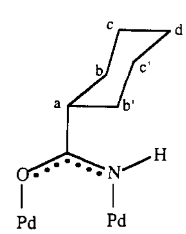


VI



VII

NMR spectra of the three amido-bridged complexes are consistent with the presence in solution of mixtures of the geometrical isomers VI and VII (see Tables I and II). Thus, the ^1H spectra show complex patterns in the H6, H6′ region, in contrast to the spectra of all the other complexes reported here, which show the comparatively simple expected pair of interpenetrating quartets (or in some cases a quartet plus a collapsed quartet resembling a singlet). The ^{13}C NMR spectra, where observable, provide much more direct evidence than the ^1H spectra for the existence in solution of the two geometrical isomers. Both $LPd_2(C_6H_{11}CONH)$ and $LPd_2(CH_2CHCONH)$ show in their ^{13}C spectra four rather than two resonances for each of the pairs of carbons C1 + C1′, C5 + C5′, C6 + C6′, and C7 + C7′; relative intensities suggest (bearing in mind the limitations upon the significance that can be attached to relative intensities in ^{13}C NMR spectra) that the two isomers are present in the $LPd_2(C_6H_{11}CONH)$ case in roughly equal proportions and in $LPd_2(CH_2CHCONH)$ in roughly 2:1 proportions. Only one resonance arising from the carboxamide carbon could be discerned in the ^{13}C spectra of both $LPd_2(C_6H_{11}CONH)$ and $LPd_2(CH_2CHCONH)$; however, in the former case, the resonance assigned to the cyclohexyl carbon directly attached to the carboxamide, namely C^a in structure VIII, was resolved into two components of approximately equal intensity, arising again from the two geometrical isomers in roughly equal proportions. Resonances arising from only one of the alkene carbons could be observed in the ^{13}C NMR spectrum of $LPd_2(CH_2CHCONH)$, namely a pair of barely resolved bands at 132.5 and 132.2 ppm in roughly 1:2 proportions, respectively. Bands corresponding to the second alkene carbon are presumed hidden under nearby L-derived bands, most likely under a conglomeration of bands, in the 121–124 ppm region arising from C2, C2′, C4, and C4′ of two isomers; any suspicion aroused by this lack of a second alkene carbon in the ^{13}C spectrum that the vinylic group has undergone some reaction or become coordinated is removed by the appearance of a three-proton ABC pattern in the normal 5.5–6.3 ppm region of the ^1H NMR spectrum.



VIII

Conjugate Base of *N*,*N*-Dimethylhydroxylamine as the Exogenous Bridge. The closely related pair of complexes $LPd_2((CH_3)_2NO)$ and $L'Pd_2((CH_3)_2NO)$, where $(CH_3)_2NO^-$ represents the conjugate base of *N*,*N*-dimethylhydroxylamine and L'^{3-} is the binucleating ligand in I, were prepared with NMR comparisons specifically in mind. Both were obtained by reaction of the appropriate acetate complex with excess *N*,*N*-dimethylhydroxylamine, but it was necessary to have present a strong base such as sodium hydroxide in the case of $LPd_2((CH_3)_2NO)$ while additional base was not required to generate $L'Pd_2((CH_3)_2NO)$. This difference, we believe, provides further evidence of the sort considered in the case of the amide-derived complexes, that the bridging site is more congested in LPd_2^+ than in $L'Pd_2^+$.

X-ray crystallographic studies of large numbers of complexes in which a thiolate sulfur center bridges two metals have revealed a strong preference for such sulfur atoms (in contrast to analogous alkoxide or phenoxide bridges) to adopt a tetrahedral arrangement with a stereochemically active lone pair of electrons occupying one tetrahedral position and two metals and a carbon center occupying the other three. This feature is apparent in the crystal structures of a number of complexes of the binucleating ligand L'^{3-}.[10,11,3,14] In these cases a consequence of the tetrahedral geometry at sulfur is that the two metal coordination planes within a molecule are considerably out of coplanarity.

Both the ^1H and the ^{13}C NMR spectra of $L'Pd_2((CH_3)_2NO)$ at room temperature indicate that the two *N*-methyl groups are in equivalent averaged environments, giving rise to a six-proton singlet at 3.21 ppm in the ^1H spectrum and a single resonance at 58.0 ppm in the ^{13}C spectrum. These results are consistent with rapid inversion at the tetrahedral sulfur as has been noted previously for the $L'Pd_2$ system.[1]

The ^1H and ^{13}C spectra of $LPd_2((CH_3)_2NO)$, in contrast, reveal two inequivalent *N*-methyl groups; two three-proton singlets at 3.05 and 3.17 ppm appear in the ^1H NMR spectrum, and in the ^{13}C NMR spectrum four peaks appear at 59.1, 58.8, 56.8, and 55.4 ppm, two of which arise from C6 + C6′ of L^{3-}, the other two arising from two inequivalent methyls of the $(CH_3)_2NO^-$ bridge. These spectra in addition clearly indicate that only one

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(14) Hoskins, B. F.; McDonald, I. A. S. *Aust. J. Chem.* **1984**, *37*, 1395.

of the two possible geometrical isomers of $LPd_2((CH_3)_2NO)$ is present in solution because in the ^1H spectrum H6 and H6′ appear as a simple superimposition of two AB quartets and in the ^{13}C spectrum there is no indication of any "doubling up" of any of the several resonances that in the amide-derived complexes did show doubling up. In $L'Pd_2((CH_3)_2NO)$ inversion at the tetrahedral sulfur generates a conformation indistinguishable from the starting conformation, so the averaged environments of the two *N*-methyl groups are the same; in $LPd_2((CH_3)_2NO)$ inversion produces an entirely new configuration and the averaged environments of the two *N*-methyl groups are different.

Experimental Section

***N*,*N*′-Bis(pyridin-2-ylmethyl)but-2-enediamide (IV).** Fumaryl chloride (35.4 g, 0.23 mol) was added to a stirred solution at 0 °C of 2-(aminomethyl)pyridine (48.2 g, 0.47 mol) in chloroform (450 mL), and the resulting mixture was stirred at 0 °C for 24 h. The somewhat discolored precipitate of the dihydrochloride of IV was collected, washed with chloroform, and dried in air (73.5 g, 87%). ^1H NMR (ppm; D_2O): 4.99 (s, 4 H, 2 CH_2); 7.13 (s, 2 H, alkene); 8.06–8.84 (m, 8 H, py). ^{13}C NMR (ppm D_2O; pyridine C's numbered as in V): 41.0 (CH_2); 125.8, 126.0 (py C2, C4); 132.5 (alkene); 141.0 (py C3); 147.3 (py C1); 152.2 (py C5); 167.0 (amide C).

Aqueous potassium carbonate (0.28 M, 1.0 L) was added to a solution of the dihydrochloride salt of IV (49.8 g, 0.14 mol). The precipitated solid was collected, washed with water, and recrystallized from methanol–water to yield colorless, crystalline IV: yield 27.6 g, 67%. ^1H NMR (ppm; $(CD_3)_2SO$): 4.47 (d, 4 H, 2 CH_2); 6.98 (s, 2 H, alkene); 9.04 (t, broad, 2 H, NH); 7.29–8.52 (m, 8 H, py). ^{13}C NMR (ppm; $(CD_3)_2SO$ (pyridine C's numbered as in V): 44.3 (CH_2); 122.2, 121.0 (py C2, C4); 132.7 (alkene); 136.7 (py C3); 148.8 (py C1); 158.0 (py C5); 163.5 (amide C). Anal. Calcd for $C_{16}H_{16}N_4O_2$: C, 64.8; H, 4.8; N, 18.9. Found: C, 64.5; H, 5.2; N, 19.1.

2-(Acetylthio)-*N*,*N*′-bis(pyridin-2-ylmethyl)butanediamide, the S-Protected Ligand V. *N*,*N*′-bis(pyridin-2-ylmethyl)but-2-enediamide (IV; 26.5 g, 0.09 mol) was dissolved in thioacetic acid (65 mL), and the mixture was heated at ca. 65 °C for 10 min. The residue left after the excess thioacetic acid had been removed under vacuum was washed thoroughly with diethyl ether to yield crude S-protected ligand V: yield 31.8 g, 95%. Recrystallization from dichloromethane–petroleum ether (bp 80–100 °C) gave 2-(acetylthio)-*N*,*N*′-bis(pyridin-2-ylmethyl)butanediamide as colorless crystals. Details of the ^1H and ^{13}C NMR spectra are considered in the Results and Discussion. Anal. Calcd for $C_{18}H_{20}N_4O_3S$: C, 58.0; H, 5.4; N, 15.0; S, 8.6. Found: C, 57.7; H, 5.2; N, 14.9; S, 8.8.

2-Mercapto-*N*,*N*′-bis(pyridin-2-ylmethyl)butanediamide. Concentrated aqueous ammonia (ca. 33% w/w, 20 mL) was added under dinitrogen to the finely powdered S-protected ligand V (1.35 g, 4.1 mmol). After a few minutes of stirring at room temperature, all the solid dissolved. After being allowed to stand at room temperature 0.5 h, the solution was evaporated to dryness below 35 °C under vacuum. The colorless solid residue was recrystallized from ethyl acetate, yielding 2-mercapto-*N*,*N*′-bis(pyridin-2-ylmethyl)butanediamide as colorless crystals (1.1 g, 90%). ^1H and ^{13}C NMR data are presented in the Results and Discussion. For the preparation of all the complexes discussed here, this separate S-deprotection step was unnecessary.

$LPd_2(CH_3CO_2)$. A solution of the S-protected ligand V (0.123 g, 0.33 mmol) in hot chloroform (2 mL) was added to a solution of palladium(II) acetate (0.148 g, 0.66 mmol) in boiling chloroform (4 mL). After a few minutes yellow needles of $LPd_2(CH_3CO_2)$ separated, which were collected, washed with chloroform, and dried in vacuo at 80 °C: yield 0.158 g, 80%. The product could be recrystallized from chloroform, but this was unnecessary. The solid absorbed water from the atmosphere. Anal. Calcd for $C_{18}H_{18}N_4O_4SPd_2{\cdot}0.5H_2O$: C, 35.5; H, 3.1; N, 9.2; Pd, 35.0. Found: C, 35.4; H, 3.0; N, 9.1; Pd, 35.2.

$LNi_2(CH_3CO_2)$. A solution of the S-protected ligand V (0.158 g, 0.42 mmol) in hot methanol (2 mL) was added to a solution of $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (0.211 g, 0.85 mmol) in hot methanol (4 mL). Fine brown needles of $LNi_2(CH_3CO_2)$ separated after a few minutes. the crystals were collected, washed with 40:60 methanol–diethyl ether and dried in vacuum at 80 °C: yield 0.123 g, 57%. The solid could be recrystallized from dichloromethane–tetrahydrofuran. The IR spectrum is essentially identical with those of $LPd_2(CH_3CO_2)$ and $LCu_2(CH_3CO_2)$. ^1H NMR data are given in Tables I and II.

$LCu_2(CH_3CO_2)$. A solution of the S-protected ligand (0.25 g, 0.68 mmol) in methanol (3 mL) was added to a boiling solution of $Cu(CH_3CO_2)_2{\cdot}H_2O$ (0.271 g, 1.36 mmol) in boiling methanol (20 mL). The resulting purple solution was evaporated to a volume of ca. 5 mL at atmospheric pressure, and the purple solid was precipitated by addition of diethyl ether. The solid was recrystallized from methanol–diethyl-ether to yield purple crystals: yield 0.203 g, 58%. Anal. Calcd for $C_{18}H_{18}N_4O_4SCu_2{\cdot}2H_2O$: C, 39.3; H, 3.3; N, 10.2; S, 5.8; Cu, 23.1. Found: C, 39.7; H, 3.6; N, 9.9; S, 6.1; Cu, 23.5.

$LPd_2(CH_3CH_2CO_2)$. $LPd_2(CH_3CO_2)$ (0.146 g, 0.24 mmol) was dissolved in propionic acid (2 mL) at 120 °C. The hot solution was filtered, and upon being cooled, the filtrate deposited yellow rodlike crystals of $LPd_2(CH_3CH_2CO_2)$, which were collected, washed with tetrahydrofuran, and dried under vacuum at 80 °C: yield 0.121 g, 70%. ^1H and ^{13}C NMR data are given in Tables I and II.

$LPd_2((CH_3)_3CCO_2)$. $LPd_2(CH_3CO_2)$ (1.13 g, 1.89 mmol) was dissolved in a boiling mixture of pivalic acid (15 mL) and dichloromethane (15 mL). The hot solution was filtered and evaporated at atmospheric pressure to ca. half the original volume, when increasing amounts of boiling ethyl acetate were added until crystallization commenced. The orange needles of $LPd_2((CH_3)_3CCO_2)$ that separated were collected, washed with ethyl acetate, and dried under vacuum at 80 °C: yield 0.788 g, 64%. ^1H and ^{13}C NMR data are given in Tables I and II.

$LNi_2((CH_3)_3CCO_2)$. A solution of pivalic acid (0.587 g, 5.74 mmol) in dichloromethane (10 mL) was added to a solution of $LNi_2(CH_3CO_2)$ (0.353 g, 0.70 mmol) in boiling dichloromethane (30 mL). The solution was evaporated at atmospheric pressure to ca. half the original volume, and an approximately equal volume of boiling petroleum ether (bp 80–100 °C) was added. The brown crystals that separated when the solution was further evaporated were collected and recrystallized from dichloromethane–petroleum ether (bp 80–100 °C): yield 2.758 g, 88%. ^1H and ^{13}C NMR data are given in Tables I and II. Anal. Calcd for $C_{21}H_{24}N_4O_2SPd_2$: C, 46.2; H, 4.4; N, 10.3; S, 5.9. Found: C, 46.4; H, 4.3; N, 10.0; S, 5.6.

$LPd_2(CF_3CO_2)$. When trifluoroacetic acid (1.5 mL, 19.6 mmol) was added to a suspension of $LPd_2(CH_3CO_2)$ (0.746 g, 1.24 mmol) in boiling dichloromethane (40 mL), the suspended solid dissolved. The hot solution was filtered and evaporated at atmospheric pressure to ca. 5 mL. Addition of ethanol produced a yellow precipitate, which was collected and recrystallized from chloroform: yield 0.679 g, 88%. ^1H NMR data are given in Table I.

$LPd_2(C_3H_3N_2)$. A solution of pyrazole (0.0169 g, 0.250 mmol) in dichloromethane (3 mL) was added to a solution of $LPd_2(CH_3CO_2)$ (0.110 g, 0.180 mmol) in dichloromethane (15 mL). The solution was evaporated at atmospheric pressure to ca. 2 mL, and boiling tetrahydroforan (5 mL) was added to the hot solution. Upon being cooled to room temperature, the solution deposited yellow crystals of $LPd_2(C_3H_3N_2)$, which were collected, washed with diethyl ether, and dried under vacuum at 80 °C: yield 0.062 g, 57%. ^1H and ^{13}C NMR data are given in Tables I and II.

$LNi_2(C_3H_3N_2)$. A solution of the S-protected ligand V (0.170 g, 0.456 mmol) and pyrazole (0.038 g, 0.55 mmol) in methanol (3 mL) was added to a solution of $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (0.231 g, 0.93 mmol) in boiling methanol (3 mL). The resulting red solution was evaporated at atmospheric pressure to ca. half the initial volume, and boiling diethyl ether (10 mL) was added. Upon being cooled to room temperature, the solution deposited red crystals of $LNi_2(C_3H_3N_2)$, which were collected, washed with ice-cold methanol and then diethyl ether, and dried under vacuum at 80 °C: yield 0.187 g, 74%. The solid could be recrystallized from dimethyl sulfoxide. ^1H and ^{13}C NMR data are given in Tables I and II. Anal. Calcd for $C_{19}H_{18}N_6O_2SNi_2{\cdot}3H_2O$: C, 40.3; H, 4.3; N, 14.8; S, 5.7; Ni, 20.8. Found: C, 40.5; H, 3.9; N, 14.8; S, 6.0; Ni, 20.9. An identical product could be obtained by reaction of $LNi_2(CH_3CO_2)$ with pyrazole in dichloromethane.

$LPd_2((CH_3)_2C_3HN_2)$. A solution of 3,5-dimethylpyrazole (0.0736 g, 0.765 mmol) in dichloromethane (5 mL) was added to a solution of $LPd_2(CH_3CO_2)$ (0.172 g, 0.286 mmol) in boiling dichloromethane (50 mL). The solution was evaporated at atmospheric pressure to ca. 5 mL, and boiling ethyl acetate (15 mL) was added. Upon being cooled to room temperature, the solution deposited yellow crystals of $LPd_2((CH_3)_2C_3HN_2)$, which were collected, washed with ethyl acetate, and dried under vacuum at 80 °C: yield 0.120 g, 66%. ^1H and ^{13}C NMR data are given in Tables I and II. Anal. Calcd for $C_{21}N_{22}N_6O_2SPd_2$: C, 39.6; H, 3.4; N, 13.2; S, 5.0. Found: C, 39.2; H, 3.7; N, 13.5; S, 5.4.

$(LPd_2(N_3)_2)Na$. A solution of sodium azide (0.066 g, 1.02 mmol) in methanol (5 mL) was added to a solution of $LPd_2((CH_3)_3CCO_2)$ (0.078 g, 0.12 mmol) in boiling methanol (20 mL). The solution was evaporated at atmospheric pressure to ca. 4 mL and then set aside to cool when $(LPd_2(N_3)_2)Na$ separated as yellow crystals, which were collected, washed with methanol, and dried under vacuum at 80 °C: yield 0.051 g, 72%. ^1H and ^{13}C NMR data are given in Table I. Anal. Calcd for $C_{16}H_{15}N_{10}O_2SNaPd_2{\cdot}H_2O$: C, 28.9; H, 2.6; N, 21.1; Na, 3.5; Pd, 32.0. Found: C, 28.5; H, 2.4; N, 21.0; Na, 4.1; Pd, 31.6.

$(LPd_2I_2)Na$. A solution of sodium iodide (0.799 g, 5.34 mmol) in acetone (15 mL) was added to a suspension of $LPd_2(CH_3CO_2)$ (0.109

g, 0.18 mmol) in acetone (200 mL). When the suspension was heated at the boiling point for ca. 5 min, all the suspended $LPd_2(CH_3CO_2)$ dissolved to give a deep orange solution. The solution was evaporated at atmospheric pressure to ca. 100 mL, when orange crystals of $(LPd_2I_2)Na$ separated. The crystals were collected, washed with acetone, and dried under vacuum at 80 °C: yield 0.092 g, 62%. Anal. Calcd for $C_{16}H_{15}I_2N_4O_2SNaPd_2 \cdot 2H_2O$: C, 22.5; H, 2.2; N, 6.6; I, 29.7; Na, 2.7. Found: C, 22.9; H, 1.9; N, 6.1; I, 29.0; Na, 2.4.

$LPd_2(SCN)$. A solution of sodium thiocyanate (0.032 g, 0.39 mmol) in water (1 mL) was added to a solution of $LPd_2((CH_3)_3CCO_2)$ (0.079 g, 0.123 mmol) in boiling methanol (20 mL). The solution was heated under reflux 3 h and was then reduced in volume by evaporation at atmospheric pressure to ca. 2 mL. On being allowed to cool and stand, the solution deposited an orange solid, which was collected, washed with methanol, and dried under vacuum at 80 °C. The solid was recrystallized from chloroform–methanol: yield 0.036 g, 49%. Anal. Calcd for $C_{17}H_{15}N_5OS_2Pd_2 \cdot H_2O$: C, 33.1; H, 2.8; N, 11.4; S, 10.4. Found: C, 32.9; H, 2.7; N, 11.4; S, 11.0.

$LPd_2(CH_3CONH)$. A solution of acetamide (0.218 g, 370 mmol) in methanol (3 mL) followed by a solution of 1,8-diazabicyclo[5.4.0]-7-undecene (dbu; 0.167 g, 1.10 mmol) in methanol (1 mL) was added to a solution of $LPd_2((CH_3)_3CCO_2)$ (0.335 g, 0.523 mmol) in boiling methanol (40 mL). The solution was evaporated at atmospheric pressure to ca. 15 mL and was then heated under reflux for 15 h, whereupon water (5 mL) was added and the volume was reduced by evaporation at atmospheric pressure until crystallization started. The yellow crystals of $LPd_2(CH_3CONH)$, which separated after the solution had cooled, were collected, washed with water and then acetone, and dried under vacuum at 80 °C: yield 0.238 g, 76%. The solid could be recrystallized from chloroform. Anal. Calcd for $C_{18}H_{19}N_5O_3SPd_2 \cdot 2.5H_2O$: C, 33.6; H, 3.8; N, 10.9. Found: C, 33.8; H, 3.4; N, 10.8.

$LPd_2(C_6H_{11}CONH)$. A solution of cyclohexanecarboxamide (0.120 g, 0.94 mmol) and 1,8-diazabicyclo[5.4.0]-7-undecene (dbu; 0.064 g, 0.42 mmol) in methanol (5 mL) was added to a solution of $LPd_2(CH_3CO_2)$ (0.143 g, 0.238 mmol) in a boiling mixture of methanol (32 mL) and dichloromethane (8 mL). The solution was heated under reflux 24 h and then filtered to remove a small amount of black precipitate. The volume was reduced by boiling at atmospheric pressure to ca. 3 mL, when yellow crystals of $LPd_2(C_6H_{11}CONH)$ separated. The crystals were collected, washed with methanol and diethyl ether, and dried under vacuum at 80 °C: yield 0.099 g, 62%. ^1H and ^{13}C NMR data are given in Tables I and II.

$LPd_2(CH_2CHCONH)$. A solution of $LPd_2(CH_3CO_2)$ (0.112 g, 0.187 mmol), 1,8-diazabicyclo[5.4.0]-7-undecene (dbu); 0.054 g, 0.35 mmol), and acrylamide (0.142 g, 1.99 mmol) in methanol (20 mL) was heated under reflux 8 h. After filtration, the solution was reduced in volume by boiling at atmospheric pressure to ca. 5 mL and boiling ethyl acetate (15 mL) was added. After further evaporation at atmospheric pressure of ca. half the solvent, orange clusters of crystals appeared. The crystals of $LPd_2(CH_2CHCONH)$ were collected, washed with ethyl acetate, and dried under vacuum at 80 °C: yield 0.052 g, 46%. ^1H and ^{13}C NMR data are given in Tables I and II. Anal. Calcd for $C_{19}H_{19}N_5O_3SPd_2 \cdot 0.5H_2O$: C, 36.9; H, 3.3; N, 11.3; S, 5.2. Found: C, 37.2; H, 3.5; N, 11.2; S, 4.9.

$LPd_2((CH_3)_2NO)$. An aqueous solution of sodium hydroxide (39 mL of a 7.76×10^{-3} M solution, 0.303 mmol) was added to a suspension of $LPd_2(CH_3CO_2)$ (0.181 g, 0.302 mmol) in boiling methanol (30 mL). After 5 min of heating ca. half the suspended solid had dissolved. *N,N*-Dimethylhydroxylamine hydrochloride (0.123 g, 1.26 mmol) dissolved in methanol (10 mL) was neutralized by passing through a column containing 5.0 g of the hydroxide form of a Dowex 200–400-mesh anion-exchange resin. The methanolic solution of *N,N*-dimethylhydroxylamine was added to the $LPd_2(CH_3CO_2)$ mixture, which had been cooled to room temperature. The solution was reheated, and all the remaining suspended $LPd_2(CH_3CO_2)$ dissolved. The volume was reduced by boiling at atmospheric pressure, selectively removing most of the methanol, until yellow crystals of $LPd_2((CH_3)_2NO)$ appeared. The solution was cooled and the product filtered, washed with acetone, and dried under vacuum at 80 °C: yield 0.123 g, 68%. The complex could be recrystallized from methanol–water. Anal. Calcd for $C_{18}H_{21}N_5O_3SPd_2 \cdot 3H_2O$: C, 33.0; H, 4.2; N, 10.7; S, 4.9. Found: C, 33.1; H, 4.5; N, 10.2; S, 5.0.

$L'Pd_2((CH_3)_2NO)$. A solution of *N,N*-dimethylhydroxylamine (0.04 g, 0.65 mmol) in methanol (10 mL) (prepared as described for $LPd_2((CH_3)_2NO)$) was added to a solution of $L'Pd_2(CH_3CO_2)$ (0.066 g, 0.093 mmol) dissolved in chloroform (10 mL). The solution turned pale yellow within seconds. Ca. 75% of the solvent was removed by boiling at atmospheric pressure. Yellow clusters of the product grew from the solution upon standing for 24 h. The product was collected, washed with methanol, and dried under vacuum at 80 °C: yield 0.045 g, 69%. Anal. Calcd for $C_{25}H_{35}O_3N_5SPd_2$: C, 43.0; H, 5.1; N, 10.0; S, 4.6. Found: C, 42.8; H, 5.3; N, 9.9; S, 4.3.

Physical Measurements. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 100 and a JEOL FX 90Q spectrometer. Infrared spectra were recorded as KBr disks on a JASCO A302 spectrophotometer. Microanalyses were performed by AMDEL, the Australian Microalytical Service, or Analytisch Laboratien, Engelskirchen, West Germany. Magnetic susceptibilities were determined by the Gouy method using tris(ethylenediamine)nickel(II) thiosulfate as calibrant. Diamagnetic corrections for the ligands were calculated by using Pascal's constants.

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