Comparative Studies on Reactions of α,β- and β,γ-Unsaturated Amides and Acids with Nickel(0), Palladium(0), and Platinum(0) Complexes. Preparation of New Five- and Six-Membered Nickel- and Palladium-Containing Cyclic Amide and Ester Complexes

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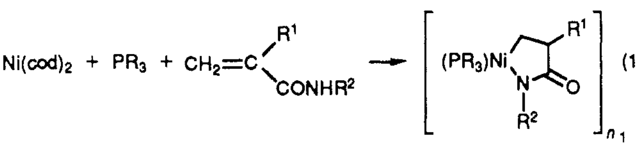
Reactivities of α,β- and β,γ-unsaturated amides as well as acids with zerovalent nickel, palladium, and platinum complexes have been compared. α,β-Unsaturated amides and acids form nickel-containing five-membered cyclic amide and ester complexes, $\overline{(PR_3)NiCH_2CH(CH_3)CONH}$ (PR_3 = PCy_3, PEt_3, $P(t\text{-}Bu)_2Et$, dppe, dppp, dppb) and $\overline{(PCy_3)NiCH_2CH(CH_3)COO}$. β,γ-Unsaturated amides and acids afford nickel-containing six-membered cyclic amide and ester complexes, $\overline{(PCy_3)NiCH_2CH_2CH_2CONH}$ and $\overline{(PCy_3)NiCH_2CH_2CH_2COO}$, whereas the palladium-containing six-membered cyclic ester complex $\overline{(PCy_3)PdCH_2CH_2CH_2COO}$ has been obtained from $Pd(PCy_3)_2$ and 3-butenoic acid. $Pt(cod)_2$ in the presence of PCy_3 reacted with methacrylamides to give olefin-coordinated Pt(0) complexes, $Pt(PCy_3)(CH_2{=}C(CH_3)CONHR)_2$ (R = H, Ph), whereas the reaction with α,β- and β,γ-unsaturated acids gave oxidative-addition products of the acids, *trans*-$PtH(O_2CR)(PCy_3)_2$ (R = $-C(CH_3){=}CH_2$, $-CH_2CH{=}CH_2$). An X-ray crystallographic analysis of one of the five-membered nickel-containing cyclic amides $[\overline{(PEt_3)NiCH_2CH(CH_3)CONH}]_4$, was carried out. A novel tetrameric cyclic structure containing a nickelacyclic amide framework linked through Ni–O bonds with adjacent amide carbonyl groups has been established. Treatment of the nickel- and palladium-containing five- and six-membered cyclic amide and ester complexes with CO liberated cyclic imides and anhydrides. Thermolysis and reactions of the nickelacyclic complexes with $AlCl_3$ and maleic anhydride led to β-elimination reactions with release of unsaturated amides and acids.

Introduction

In comparison to metallacyclic alkanes, which have attracted considerable attention,[2] the chemistry of metallacycles containing N or O atoms has attracted less attention.[3] We previously reported the preparation of five-membered nickel-containing cyclic amide and ester complexes by reactions of α,β-unsaturated amides and carboxylic acids with Ni(0) complexes coordinated with bulky and basic tertiary phosphine ligands:[4]



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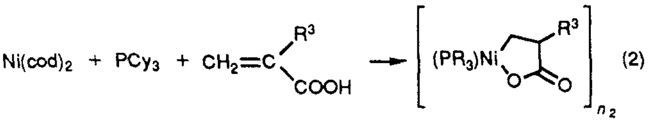
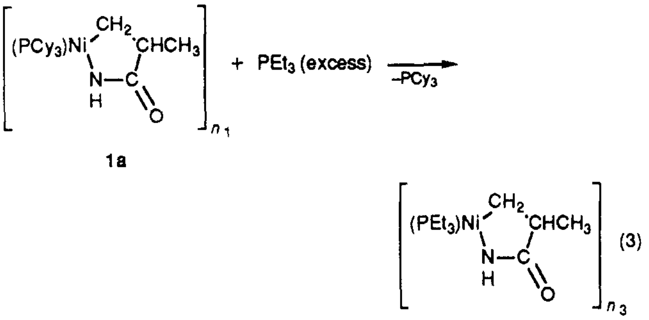
cod = 1,5-cyclooctadiene
PR_3 = PCy_3 (tricyclohexylphosphine), $P(t\text{-}Bu)_2Et$
R^1 = H, CH_3; R^2 = H, CH_3, C_6H_5 (**1a**: PR_3 = PCy_3, R^1 = CH_3, R^2 = H)
n_1 not determined



R^3 = H, CH_3
n_2 not determined

It has been further revealed that the bulky tertiary phosphine ligand in **1** can be readily replaced by triethylphosphine, PEt_3, to give a PEt_3-coordinated metallacycle:



The nickel-containing cyclic amides and esters have been characterized on the basis of elemental analysis, NMR and IR spectroscopy, and their chemical properties, but no X-ray data have been supplied. On the basis of the molecular weight determination by a cryoscopic method in

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(2) (a) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (b) Puddephatt, R. *Coord. Chem. Rev.* **1980**, *33*, 149. (c) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Able, E. W., Eds.; Pergamon Press: New York, 1982.

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Table I. Selected Bond Distances and Angles of $[(Et_3P)\overline{Ni(NHCOCH(Me)CH_2)}]_4$

Bond Distances (Å)

Ni1–O10	1.919 (7)	Ni1–N13	1.930 (12)	Ni1–C17	1.933 (10)	Ni1–P5	2.152 (4)
Ni2–O11	1.928 (7)	Ni2–N14	1.908 (10)	Ni2–C18	1.956 (10)	Ni2–P6	2.127 (4)
Ni3–O12	1.942 (8)	Ni3–N15	1.921 (8)	Ni3–C19	1.974 (12)	Ni3–P7	2.143 (3)
Ni4–O9	1.952 (9)	Ni4–N16	1.882 (8)	Ni4–C20	1.939 (13)	Ni4–P8	2.135 (3)

Bond Angles (deg)

O10–Ni1–N13	91.4 (4)	O10–Ni1–C17	171.4 (4)	N13–Ni1–C17	84.1 (5)
O11–Ni2–N14	91.3 (3)	O11–Ni2–C18	172.2 (5)	N14–Ni2–C18	85.0 (4)
O12–Ni3–N15	91.3 (4)	O12–Ni3–C19	170.1 (4)	N15–Ni3–C19	84.5 (4)
O9–Ni4–N16	91.0 (4)	O9–Ni4–C20	173.6 (4)	N16–Ni4–C20	86.0 (4)
P5–Ni1–N13	171.2 (3)	P5–Ni1–C17	89.2 (4)	P5–Ni1–O10	95.9 (3)
P6–Ni2–N14	171.7 (3)	P6–Ni2–C18	89.6 (4)	P6–N2–O11	94.9 (3)
P7–Ni3–N15	174.4 (3)	P7–Ni3–C19	89.2 (3)	P7–Ni3–O12	95.7 (2)
P8–N24–N16	174.4 (3)	P8–Ni4–C20	89.0 (4)	P8–Ni4–O9	94.3 (3)

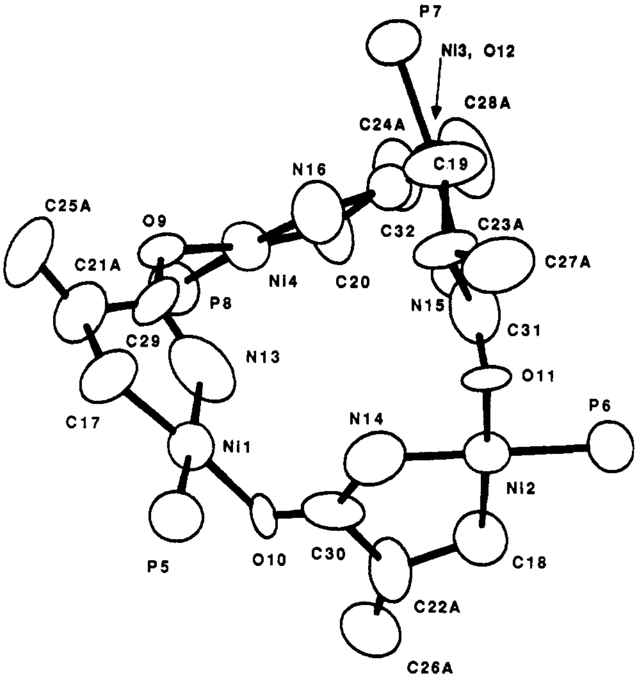

Figure 1. Molecular structure of $[(PEt_3)\overline{NiCH_2CH(CH_3)CONH}]_4$ (2). Carbon atoms of PEt_3 ligands are omitted for simplicity. For the disordered carbon atoms one of the two coordinates is shown.

benzene as well as NMR spectroscopic data, a trimeric cyclic structure ($n_3 = 3$) bridged through Ni–N bonds has been tentatively proposed for 2.[4] We now report the results of an X-ray structural analysis of the PEt_3-coordinated complex 2 together with some chemical properties of the five-membered metallacycles.

The natural extension of the chemistry of the five-membered nickel-containing metallacycles is to explore the possibility of formation of six-membered metallacycles and to examine if one can prepare the corresponding palladium and platinum analogues. The results of these attempts are also reported here.

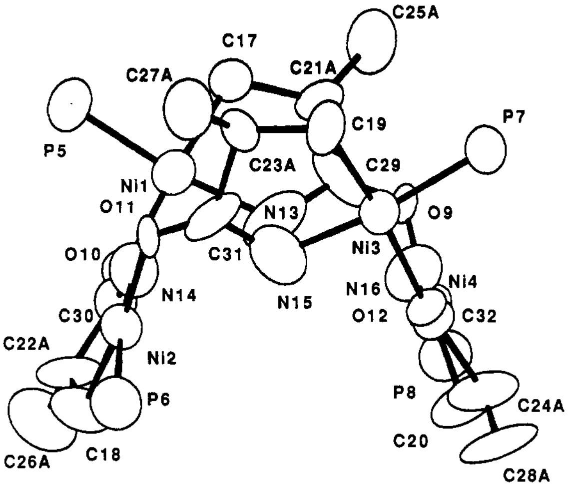

Figure 2. Another view of 2. Carbon atoms of PEt_3 ligands are omitted for simplicity. For the disordered carbon atoms one of the two coordinates is shown.

Results and Discussion

Structure of $[\{P(C_2H_5)_3\}\overline{NiCH_2CH(CH_3)CONH}]_4$ (2) and Chemical Properties of the Nickel-Containing Five-Membered Cyclic Amide Complexes. The PEt_3-coordinated nickel-containing cyclic amide 2 prepared by reaction 3 gives yellow air-sensitive triclinic crystals, which were subjected to X-ray measurements.

The molecular structure of 2, shown in Figures 1 and 2, reveals a tetrameric cyclic structure composed of a 16-membered cagelike macrocycle containing four crystallographically independent $(Et_3P)\overline{NiCH_2CHMeCONH}$ units. Each metallacycle unit is bonded to an adjacent nickel atom in another unit through the amide carbonyl oxygen, not through the amide nitrogen as previously assumed.[4b] Four nitrogen atoms in this molecule form a plane, and a large vacancy is present in the center of the plane.

Figure 3 shows the structure of one of the nickel-containing cyclic amide units. Four ligating atoms (P, C, O, and N) have a slightly distorted square-planar coordination around the metal center. Table I summarizes selected bond distances and angles. The CH and CH_3 carbon atoms in the metallacyclic amide units are disordered with 50% probabilities. Two pairs of disordered CH and CH_3 carbon atoms in each metallacycle unit correspond to the structure with different configurations of the asymmetric CH carbon.

From these crystallographic results we cannot exclude completely a structure with a C=C double bond such as $[(PEt_3)\overline{NiCH_2C(=CH_2)CONH}]_4$. However, the ^{13}C NMR spectrum of 2 shows signals for CH, CH_3, and CH_2 carbons

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(3) (a) Omae, I. *Organometallic Intramolecular-coordination Compounds*; J. Organomet. Chem. Libr. 18; Elsevier: Amsterdam, 1986; p 402. (b) Hoberg, H.; Summermann, K.; Milehereit, A. *J. Organomet. Chem.* **1985**, *288*, 327. (c) Hoberg, H.; Oster, B. W. *Ibid.* **1982**, *234*, C35. (d) Uhlig, V. E.; Walther, D. *Coord. Chem. Rev.* **1980**, *33*, 3. (e) Jenni, K.; Hoberg, H. *J. Organomet. Chem.* **1987**, *322*, 193. (f) Hernandez, E.; Hoberg, H. *Ibid.* **1987**, *327*, 429; **1987**, *328*, 403. (g) Hoberg, H. *Ibid.* **1988**, *358*, 507. (h) Carmona, E.; Gutiérrez-Puebla, E.; Marin, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1980**, *102*, 7448.

(4) (a) Yamamoto, T.; Igarashi, K.; Ishizu, I.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1979**, 554. (b) Yamamoto, T.; Igarashi, K.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 7448.

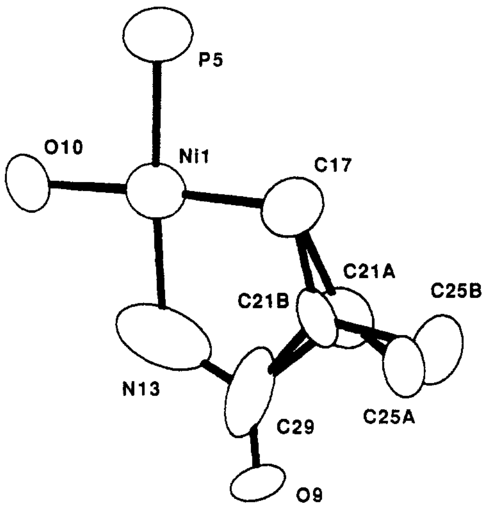
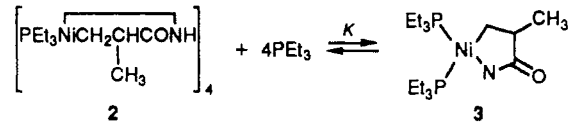


Figure 3. Drawing of a $(PEt_3)\overline{NiCH_2CH(CH_3)CONH}$ unit in 2. C21A, C21B, C25A, and C25B are disordered positions of the carbon atoms with 50% probabilities.

with reasonable chemical shifts and J(CH) values for the proposed structure (see Experimental Section).[5]

The $^{31}P\{^1H\}$ NMR spectrum of the nickel-containing cyclic amide 2 shows a complex pattern reflecting the tetrameric structure, but addition of excess PEt_3 to 2 gives the appearance of new two doublets in addition to the $^{31}P\{^1H\}$ NMR signal of 2 at −30 °C (Figure 4). The relative ratio of the peak areas of the signals due to 2 and those of the two doublets decreases on lowering the temperature. At −80 °C only the two doublets are observed. The two doublets are considered to arise from the metallacycle complex 3, containing two magnetically inequivalent PEt_3 ligands, and the variation of the spectrum with temperature suggests the involvement of the equilibrium



(4)

From the relative ratios of the integrated areas of the respective peaks arising from 2, 3, and free PEt_3 in the $^{31}P\{^1H\}$ NMR spectra at various temperatures, the equilibrium constants $K = [3]^4/[2][PEt_3]^4$ have been estimated as follows: $K = 0.26$ dm^3 mol^{-1} (273 K), 1.5 dm^3 mol^{-1} (263 K), 7.4 dm^3 mol^{-1} (258 K), and 84 m^3 mol^{-1} (243 K). The following thermodynamic parameters for the equilibrium have been derived from the temperature dependence of the equilibrium constants: $\Delta H_{263} = -107$ kJ mol^{-1}, $\Delta S°_{263} = -403$ J K^{-1} mol^{-1}, and $\Delta G°_{263} = -1$ kJ mol^{-1}.

As reported previously,[4b] 1,2-bis(diphenylphosphino)ethane (dppe) as the ditertiary phosphine ligand readily displaces the tricyclohexylphosphine ligand in 1 to give the dppe-coordinated nickelacycle 4, which proved to be monomeric by vapor-pressure osmometry. We have extended the study to prepare a series of nickelacycles having ditertiary phosphine ligands employing 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb) and obtained the metallacycles containing five- to seven-membered chelate rings:

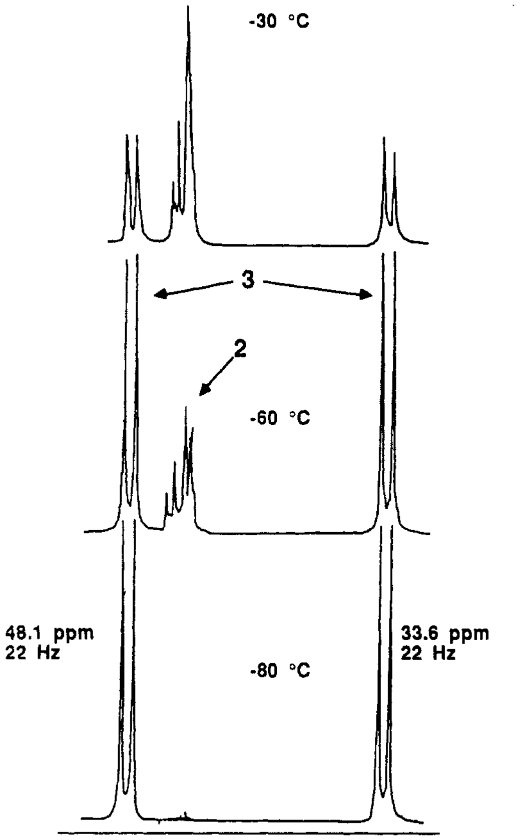
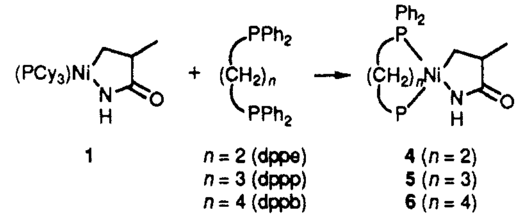


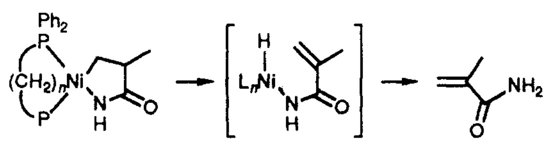
Figure 4. $^{31}P\{^1H\}$ NMR spectra of a mixture of 1a and PEt_3 (1.17:1.00) at −30, −60, and −80 °C in CD_2Cl_2. The peak of free PEt_3 is omitted.



(5)

The analytical and spectroscopic data are summarized in Table II. The spectroscopic data for the dppp- and dppb-coordinated complexes are compatible with mononuclear structures.

The thermal stability of the chelating diphosphine-coordinated complexes decreased with an increase in the chelate ring size (Table III summarizes the results of various reactions). The dppe-coordinated complex 4 had the highest decomposition temperature, 210 °C, which decreased to 190 °C for the dppp complex 5 and 170 °C for the dppb complex 6. The only thermolysis product of 4 was methacrylamide (82%), which was formed by a β-elimination process:



(6)

On thermolysis of the nickelacycles the dppp- and dppb-coordinated complexes released some 2-methylpropanamide, the hydrogenation product of methacrylamide, in addition to the simple β-elimination product. The hydrogen source is not clear, a possible cause being the ortho metalation of the phosphine ligands. No reductive-elimination product, β-lactam, was detected.

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[5] We conclude that the tetrameric structure confirmed in the solid state by X-ray crystallography is maintained also in the solution on the basis of the good linearity of the van't Hoff plot of eq 4, although we do not have sufficient experimental evidence to exclude other structures completely. Previously, we tentatively assumed the trimeric structure on the basis of cryoscopy. However, it is a difficult task to obtain an accurate molecular weight of a compound having high molecular weight by this method.

Table II. Analytical and Spectral Data for Isolated Metallacycle Complexes

complex	mp, °C	anal. found (calcd), % C	H	N	IR,[a] cm^{-1}	^1H NMR,[b] δ	$^{13}C\{^1H\}$ NMR,[c] ppm	$^{31}P\{^1H\}$ NMR,[d] ppm
5	185–190 dec	66.5 (66.9)	6.2 (5.9)	2.5 (2.5)	1590* 1435 1095 690	0.4 (1 H, br), 0.8 (3 H, d, 7 Hz), 1.2–2.6 (8 H, br), 5.0 (1 H, br), 7.4–8.0 (20 H)	22.8 (s, *C*H_3), 25.2 (s, dppp), 30.3 (d, 22 Hz, Ni–*C*), 31.8 (dd, 25 and 9 Hz, dppp), 37.0 (dd, 57 and 20 Hz, dppp), 45.2 (s), 128–134 (m), 197.8 (d, 13 Hz, *C*=O)	12.6 (d, 34 Hz), 33.8 (d, 34 Hz)
6	170 dec	67.4 (67.4)	6.2 (6.1)	2.6 (2.5)	1595* 1430 1090 690	0.8 (1 H, br), 1.0–2.5 (11 H, br), 3.6 (1 H, br), 7.3–7.6 (20 H)	21.3 (dd, 7 and 3 Hz, CH_3), 23.8 (s, dpb), 24.6 (s, dppb), 27.3 (d, 17 Hz, dppb), 28.8 (dd, 21 and 6 Hz, dppb), 34.2 (dd, 56 and 21 Hz, Ni–*C*), 41.6 (s), 128–134 (m), 193 (d, 15 Hz, *C*=O)	31.9 (d, 17 Hz), 39.1 (d, 17 Hz)
7	210–215 dec	61.9 (62.3)	9.7 (9.4)	3.1 (3.3)	2920 2850 1560* 1445			
8	155–160 dec	61.9 (62.2)	9.5 (9.2)		2920 2850 1580* 1445			
9	180–185 dec	55.4 (55.9)	8.7 (8.3)		2920 2850 1570* 1445			
10	194–196	48.0 (48.3)	7.7 (7.4)	4.2 (4.3)	3400 3370 1650* 1590			
11	215–216	57.6 (57.2)	7.2 (6.9)	3.5 (3.5)	3300 2920 2850 1680* 1660*			
12	245–247	57.0 (57.0)	9.1 (8.7)		2920 2850 2250** 1640 1590*	−22.7 (1 H, t, 14 Hz, *J*(H–Pt) = 1143 Hz, Pt–H), 1.2–2.0 (66 H, PCy_3), 5.1 (1 H, s), 5.7 (1 H, d, 3 Hz)	20.5 (s, *C*H_3), 27.0 (s, PCy_3), 28.0 (t, 5 Hz, PCy_3), 30.5 (t, 15 Hz, PCy_3), 35.1 (t, 13 Hz, PCy_3), 118.5 (s, =*C*H), 144.3 (s), 171.7 (s, *C*=O)	46.7 (*J*(P–Pt) = 2919 Hz)
13	154–155	56.8 (57.0)	9.0 (8.6)		2920 2850 2220** 1640 1590*	−22.9 (1 H, t, 14 Hz, *J*(H–Pt) = 1146 Hz, Pt–H), 1.2–2.0 (66 H, PCy_3), 3.0 (2 H, d, 7 Hz), 4.9 (1 H, d, 16 Hz), 5.0 (1 H, d, 5 Hz), 6.7 (1 H, m)	27.0 (s, *C*H_3), 28.0 (t, 5 Hz, PCy_3), 30.5 (t, 15 Hz, PCy_3), 35.1 (t, 14 Hz, PCy_3), 43.8 (t, 7 Hz), 114.3 (s, =*C*H), 136.8 (s), 174.5 (s, *C*=O),	46.5 (*J*(P–Pt) = 2916 Hz)

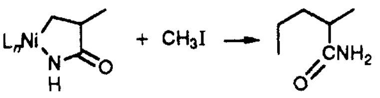
[a] The bands with one and two asterisks are assigned to ν(C=O) or amide I and ν(Pt—H), respectively. [b] In CD_2Cl_2 at room temperature: s = singlet, d = doublet, t = triplet, and br = broad. [c] In CD_2Cl_2 at room temperature; from internal TMS. See footnote *b* for abbreviations. [b] In CD_2Cl_2 at room temperature; from external PPh_3.

Table III. Chemical Reactivities of Complexes

complex	type of reacn or reactant[a]	reactant: complex[b]	temp,[c] °C	time, h	solvent	product (% yield of complex)
4	thermolysis		210	3	none	methacrylamide (82)
5	thermolysis		190	3	none	methacrylamide (27), 2-methylpropanamide (7)
6	thermolysis		170	3	none	methacrylamide (39), 2-methylpropanamide (16)
7	thermolysis		210	3	none	3-butenamide (64), 2-butenamide (6)
4	$AlCl_3$	1.0	room temp	24	CH_2Cl_2	methyacrylamide (73)
4	MAH	1.0	room temp	24	CH_2Cl_2	methacrylamide (29), 2-methylpropanamide (20)
7	MAH	1.0	room temp	24	THF	3-butenamide (61)
14[d]	MAH	4.0	40	0.1	CH_2Cl_2	3-butenoic acid (97)
1a	CH_3I	excess	110	5	toluene	2-methylbutanamide (93)
2	CH_3I	excess	65	5	THF	2-methylbutanamide (100)
4	CH_3I	excess	65	5	THF	2-methylbutanamide (57)
15[d]	CH_3I	excess	room temp	36	CH_2Cl_2	methyl 3-methylbutenate (41)
7	CO	excess (1 atm)	room temp	1	THF	glutarimide (66), $Ni(CO)_3(PCy_3)$[e]
8	CO	excess (1 atm)	room temp	24	hexane: –THF	glutaric anhydride (24), $Ni(CO)_3(PCy_3)$[e]
9	CO[f]	excess (1 atm)	room temp	2	THF	gluraric anhydride (10)
12	CO	excess (1 atm)	room temp	10	THF	methylacrylic acid (29)

[a] MAH = maleic anhydride. [b] Molar ratio. [c] Room temp = room temperature. [d] 14 = $(bpy)\overline{NiCH_2CH_2CH_2COO}$; 15 = $(PCy_3)\overline{NiCH_2CH(CH_3)COO}$. [e] Formation of $Ni(CO)_3(PCy_3)$ was confirmed by IR spectroscopy; however, its amount was not measured. [f] Reaction in the presence of bpy (see text).

The β-elimination reaction of the nickel-containing cyclic amide was promoted by addition of $AlCl_3$ to 4. A similar promotion effect for the β-elimination was observed when maleic anhydride was added as a π-acid to 4; the process entailed the formation of the hydrogenation product of methacrylamide. Treatment of the nickel-containing five-membered cyclic amides **1**, **2**, and **4** with methyl iodide selectively gave 2-methylbutanamide, the methylation product at the nickel-bound carbon:

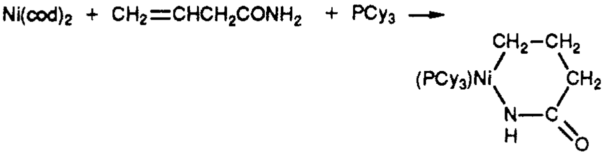


(7)

L = PCy_3, PEt_3, dppe

Hoberg and Oster reported the occurrence of a similar methylation reaction on treatment of their nickelacyclic amide complexes with methyl iodide.[3b]

Preparation of Six-Membered Metallacycles and Their Chemical Reactions. Metallacycle formation quite similar to that observed with α,β-unsaturated amides and acids occurred in the reactions of the Ni(0) complex with β,γ-unsaturated amides and acids to afford six-membered nickelacycles:



(8)

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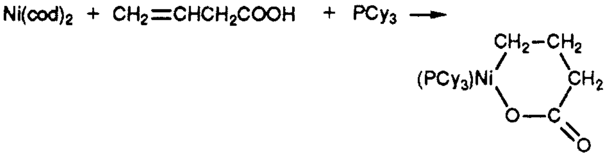
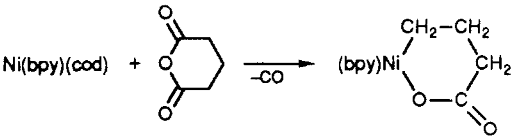


(9)

8

These six-membered-ring structures for 7 and 8 have been confirmed by their chemical properties. Complexes 7 and 8 react with CO to give the six-membered cyclic imide and anhydride, respectively (vide infra). Reaction of 8 with dppe in CS_2 solution gives the previously reported $(dppe)\overline{NiCH_2CH_2CH_2COO}$, having a six-membered cyclic structure.

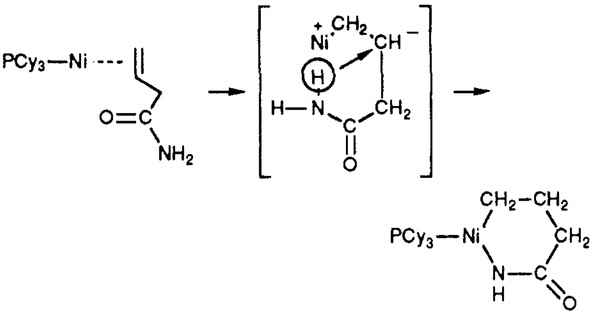
A six-membered nickel-containing cyclic ester similar to 8, but having a bipyridine ligand (bpy), was prepared previously by treating Ni(bpy)(cod) with glutaric anhydride in a process accompanied by decarbonylation:[6]



(10)

Table II contains analytical and spectroscopic data for complexes 7 and 8. The IR spectra of the six-membered complexes 7 and 8 resemble those of the PCy_3-coordinated nickel-containing five-membered cyclic amide and ester complexes. The IR spectrum of 7 shows a very weak ν(N–H) band. A reaction similar to eq 9 with perdeuterated cyclohexylphosphine, PCy_3-d_{33}, gave the PCy_3-d_{33}-coordinated cyclic ester complex 8-d_{33}.

Two pathways are conceivable for formation of the metallacycles. One is initial oxidative addition involving the cleavage of the N—H or O—H bond accompanying formation of a nickel hydride, into which the C=C double-bond inserts. The other is initial coordination of the β,γ-unsaturated compounds through the C=C double bond to nickel followed by proton migration:



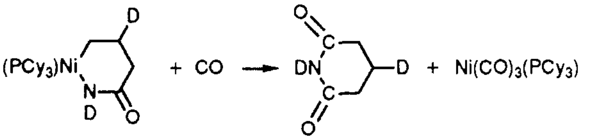
(11)

7

Use of CH_2=$CHCH_2COND_2$ in reaction 8 gave $(PCy_3)\overline{NiCH_2CHDCH_2COND}$ (7-d_2). Similarly, treatment of $Ni(cod)_2$ with CH_2=$CHCH_2COOD$ in the presence of PCy_3 in reaction 9 afforded $(PCy_3)\overline{NiCH_2CHDCH_2COO}$ (8-d_1). Complexes 7 and 8 are insoluble in weakly coordinating solvents such as tetrahydrofuran, CH_2Cl_2, and acetone, presumably due to formation of polymeric species through intermolecular coordination of the amide and ester groups with the neighboring nickel atom in a manner similar to that for the tetrameric complex 2. They dissolve in pyridine, a more strongly coordinating solvent, which induces skeletal isomerization with ring contraction (vide infra).

The IR ν(C=O) band of 7 is observed at 1560 cm^{-1}, which is close to the band of the five-membered tetrameric nickel-containing cyclic amide complex 2 at 1572 cm^{-1} and different from the ν(C=O) band of the monomeric dppe-coordinated complex 4 at 1600 cm^{-1}.

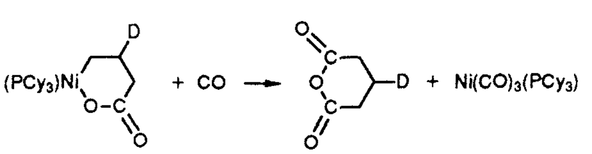
One of the typical characteristics in reactions of these types of metallacycles is their propensity under CO to undergo insertion followed by reductive elimination of cyclic imides or cyclic acid anhydrides. The nickelacyclic amide 7 in THF readily reacts at room temperature with CO at 1 atm to give glutarimide and $Ni(CO)_3(PCy_3)$ (Table III). The deuterated complex 7-d_2 selectively gave glutarimide-d_2 (as labeled below) in 66% yield on treatment with CO:



(12)

7-d_2

The nickel-containing cyclic ester complex 8 similarly underwent the CO insertion and reductive elimination to produce glutaric anhydride and $Ni(CO)_3(PCy_3)$. The deuterated complex 8-d_1 gave the deuterated glutaric anhydride-d_1 (as labeled below):



(13)

8-d_1

Thermolysis of the nickelacyclic amide 7 liberated mainly the β-elimination product, 3-butenamide, accompanied by formation of its isomerized product 2-butenamide.

While the metallacyclic ester 8 is insoluble in weakly

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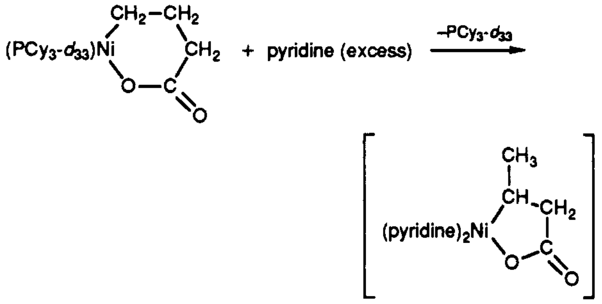
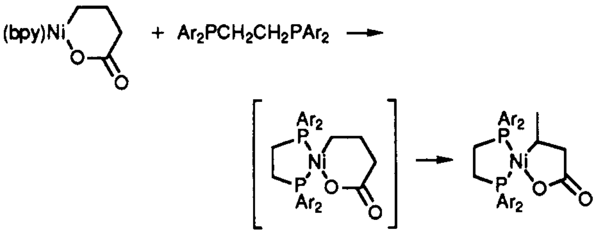
[6] Sano, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2741.

coordinating solvents, it dissolves slowly in pyridine with replacement of the PCy_3 ligand. The ^1H and $^{31}P\{^1H\}$ NMR spectra obtained in situ after complete dissolution of **8** indicates the formation of a five-membered nickel-containing cyclic ester formulated as $(py)_n\overline{NiCH(CH_3)CH_2COO}$.[7] These results indicate that rapid ring contraction of the six-membered nickel-containing cyclic ester to the five-membered isomer occurs during dissolution of the complex in pyridine:



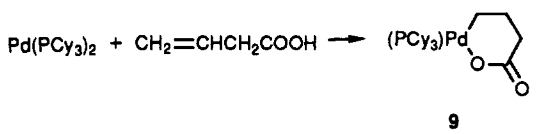
(14)

A similar ring-contraction reaction was observed in the displacement of the bipyridine ligand in $(bpy)\overline{NiCH_2CH_2CH_2COO}$, obtained by reaction 10, with achiral and chiral ditertiary phosphine ligands:[6,8]



(15)

Palladium-Containing Cyclic Ester. Treatment of $Pd(PCy_3)_2$ with methacrylamide and acrylic acid gave no isolable complex having the metallacylic entity. On the other hand, reaction of $Pd(PCy_3)_2$ with 3-butenoic acid afforded a new palladium-containing six-membered cyclic ester complex, which represents the first Pd-containing nickel analogue of this type:[9]

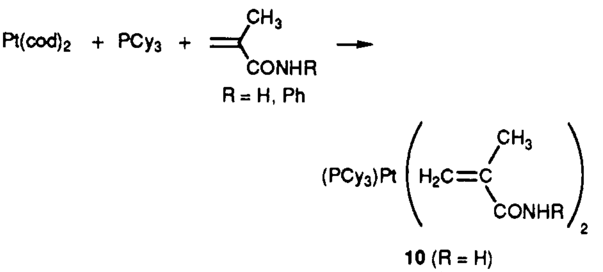


(16)

9

The IR spectrum of the palladium metallacycle **9** is almost superimposable with that of its nickel analogue **8**. Treatment of **9** with CO in the presence of bipyridine released glutaric anhydride (10%). The low yield may be a reflection of the reactivity of the palladium complex with CO being generally lower than that of nickel complexes.[10]

Reactions of Unsaturated Amides and Carboxylic Acids with a Platinum(0) Complex. The behavior of $Pt(cod)_2$ differs from that of $Ni(cod)_2$ or $Pd(PCy_3)_2$ in that no platinacycle could be prepared on its treatment with α,β- or β,γ-unsaturated amides or acids, whereas a platinacycle was obtained by treatment with succinic anhydride.[11] Reactions with methacrylamide and *N*-phenylmethacrylamide with $Pt(cod)_2$ in the presence of PCy_3 led to the formation of π-complexes:

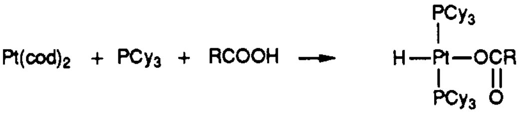


(17)

10 (R = H)
11 (R = Ph)

The IR spectrum of **10** shows two ν(N—H) bands at 3370 and 3200 cm^{-1} and two ν(C=O) bands of the amide group at 1650 and 1590 cm^{-1}. The spectrum suggests that methacrylamide is bonded to platinum through the C=C double bond and the amide group remains uncoordinated,[4,12] although the NMR data are not obtainable due to the insolubility of **10** in organic solvents. Whereas the nickel analogue of **10** underwent cyclization on heating to give a nickel-containing cyclic amide[4] with liberation of 1 equiv of olefin, no such reaction was observed with the platinum π-complexes. These π-complexes **10** and **11** did not react with CO, whereas the nickel analogues liberate the coordinated olefins to form CO-coordinated complexes.

On the other hand, when $Pt(cod)_2$ was treated with α,β- and β,γ-unsaturated acids in the presence of PCy_3, no π-complex formation was observed.[13] Instead, methacrylic acid and 3-butenoic acid oxidatively added to the Pt(0) complex to produce *trans*-hydrido(carboxylato)platinum(II) complexes:



$$Pt(cod)_2 + PCy_3 + RCOOH \longrightarrow H\text{—}\underset{PCy_3}{\overset{PCy_3}{Pt}}\text{—}O\overset{}{\underset{O}{\overset{}{\underset{\|}{C}}}}R \qquad (18)$$

12 (R = $-C(CH_3){=}CH_2$)
13 (R = $-CH_2CH{=}CH_2$)

The ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **12** and **13** showed little shift of the olefinic protons and carbons, excluding the possibility of coordination of the C=C double bond in the carboxylato ligand to platinum. The hydride signal is observed as a triplet with ^{195}Pt satellites in accordance with the trans configuration. The ν(C=O) bands are observed at frequencies higher than 1600 cm^{-1} in the IR spectra of **12** and **13**, indicating that the carboxylato ligands are bonded to Pt through one oxygen atom.

Treatment of complex **12** with CO slowly liberates methacrylic acid (Table III), and no methylsuccinic anhydride was formed. Complexes **12** and **13** show high thermal stability, and no cyclization involving the insertion of the C=C double bond into the Pt—H bond has been observed on heating of **12** and **13** in boiling organic solvents such as toluene.

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(7) NMR (^1H and $^{31}P\{^1H\}$) spectra of the solution of **8**-d_{33} in pyridine-d_5 measured in situ indicate the formation of a five-membered nickel-containing cyclic ester complex formulated as $(py)_n\overline{NiCH(CH_3)CH_2COO}$. $^{31}P\{^1H\}$ NMR spectroscopy shows complete liberation of PCy_3 from the nickel center. ^1H NMR: δ 0.59 (d, 3 H, *J*(HH) = 7 Hz, C*H*$_3$), 2.08 (dd, 1 H, *J*(HH) = 5 and 16 Hz, CH*H*), 3.06 (dd, 1 H, *J*(HH) = 7 and 16 Hz, CH*H*). The signal due to the methine hydrogen is overlapped with the PCy_3 signal.

(8) Yamamoto, T.; Sano, K.; Yamamoto, A. *J. Am. Chem. Soc.* **1987**, *109*, 1092.

(9) A preliminary communication was published: Sano, K.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1982**, 695.

(10) E.g.: Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.

(11) Sano, K.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1983**, 115.

(12) (a) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350. (b) Kubo, Y.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1973**, *59*, 353.

(13) The result was briefly reported previously in communication form: Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett.* **1982**, 907.

Conclusions

Examination of reactivities of the zerovalent nickel, palladium, and platinum complexes toward α,β- and β,γ-unsaturated amides and acids revealed that the nickel complex has the highest propensity to form metallacyclic amides and esters. The isolated nickel-containing five- and six-membered cyclic amide and ester complexes readily undergo CO insertion and subsequent reductive elimination to generate five- and six-membered cyclic imides and anhydrides. Although direct comparison with $\mathrm{Pd(cod)_2}$ was not made because of its thermal instability, the related zerovalent palladium complex $\mathrm{Pd(PCy_3)_2}$ showed much less reactivity toward the unsaturated amides and acids. Only in one case was a palladium-containing six-membered cyclic ester complex (**9**) obtained. The platinum analogue $\mathrm{Pt(cod)_2}$ gave no metallacycle but afforded olefin-coordinated complexes **10** and **11** as well as oxidative-addition products **12** and **13**. These results imply that the initial coordination of the double bond followed by polarization as shown in eq 11 may be an important factor in inducing the metallacycle formation. The suitability of the Ni(0) complex for the metallacycle formation compared to that of Pd(0) and Pt(0) complexes may arise from its favorable π-bond formation between the metal and the olefins.[12]

Experimental Section

Materials and Manipulation. $\mathrm{PCy_3}$,[14] dppp,[15] dppb,[15] 3-butenamide,[16] $\mathrm{Ni(cod)_2}$,[17] *N*-phenylmethacrylamide, $\mathrm{Pt(cod)_2}$,[18] and $\mathrm{Pd(PCy_3)_2}$[19] were synthesized by the methods given in the literature. 3-Butenamide-*N,N*-d_2 and 3-butenoic acid-*d* were prepared by repeated H–D exchange of 3-butenamide and 3-butenoic acid, respectively, with $\mathrm{D_2O}$. Other reagents were purchased from Tokyo Kasei Co. Ltd. or Wako Chemicals Co. Ltd. Complexes **1a** and **2** were prepared as previously reported.[4b] Solvents were dried by the usual methods, distilled under $\mathrm{N_2}$, and stored under $\mathrm{N_2}$. Preparation, recrystallization, and reactions of the complexes were carried out under deoxygenated $\mathrm{N_2}$ or Ar.

Elemental Analysis and Measurement of IR and NMR Spectra. Microanalyses of C, H, and N were performed by Mr. T. Saito in our laboratory with a Yanagimoto CHN Type MT-2 autocorder. Products of the reactions listed in Table III were analyzed with a Shimadzu GC-3BT and GC-6A gas chromatogram and a Hitachi M-80 GC–MS analyzer. IR spectra were recorded on a Hitachi Model 295 infrared spectrophotometer, ^{1}H NMR spectra on a Japan Electron Optics Laboratory (JEOL) Model JNM-PS-100 spectrometer, and ^{31}P and ^{13}C NMR spectra on JEOL Model JNM-FX-100 and JNM-GX-500 Fourier transform spectrometers.

Analysis of Crystal Structure. Single crystals of $[(\mathrm{Et_3P})\overline{\mathrm{NiCH_2CH(Me)CONH}}]_4$ (**2**; 0.30 × 0.30 × 0.45 mm) were grown from hot hexane and sealed in glass capillary tubes under argon. Crystal data: $\mathrm{C_{40}H_{88}N_4O_4Ni_4P_4}$; $M_r = 1047.2$; triclinic; space group $P\bar{1}$; $a = 12.084$ (3) Å, $b = 20.335$ (4) Å, $c = 11.896$ (2) Å, $\alpha = 96.95$ (2)°, $\beta = 90.53$ (2)°, $\gamma = 101.6$ (2)°, $V = 2762.8$ (1.2) Å^3; graphite-monochromated Mo Kα radiation, $\lambda = 0.71068$ Å; $\mu = 39.6$ cm^{-1}; $D_{\mathrm{calcd}} = 1.26$ g cm^{-3}, $D_{\mathrm{obsd}} = 1.31$ g cm^{-3} (flotation in a $\mathrm{CCl_4}$–hexane mixture); $F(000) = 984$.

Cell dimensions and their standard deviations were obtained from least-squares calculations of 2θ values of 25 reflections with 2θ near 20°. Intensity data were collected on a Rigaku AFC-5 four-cycle automated diffractometer by the ω–2θ scan method at a scan rate of 4° min^{-1}. Among 9640 independent reflections measured to $2\theta = 50°$, 6381 reflections with $|F_o| > 3\sigma(F_o)$ were used in structure calculations.

The structure of the molecule was determined by common Fourier methods. A full-matrix least-squares procedure was applied to refine the structure with anisotropic temperature factors for all the non-hydrogen atoms. Thermal ellipsoids of CH and $\mathrm{CH_3}$ carbons indicated possible disorder. The best model has disorder of all the CH and $\mathrm{CH_3}$ carbons in the nickel-containing cyclic amide moiety. Positions of these disordered carbon atoms were refined with 50% probability for each position. The probabilities were not refined. Hydrogen atoms were not included in the least-squares calculations. Final R and R_w values were 0.086 and 0.071, respectively ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, where $1/w = \sigma(F_o)^2 + 0.0009(F_o)^2$).

All calculations were carried out by the program system CRYSTAN on a FACOM A-70 computer.

^{13}C NMR spectra of **2** confirmed the above structure rather than the structure $[(\mathrm{PEt_3})\overline{\mathrm{NiCH_2C({=}CH_2)CONH}}]_4$, which could not be excluded completely from the X-ray results.[20] ^{13}C{^{1}H} NMR (500 MHz at 25 °C in $\mathrm{CD_2Cl_2}$): δ 43.2–42.5 (m, *C*HCH$_3$), 22.8–21.6 (m, *C*H$_3$CH), 13.5–13.0 (m, (CH$_3$*C*H$_2$)$_3$P), 10.4–9.6 (m, Ni*C*H$_2$), 8.2–8.0 (m, (*C*H$_3$CH$_2$)$_3$P).

Preparation of Complexes. $\mathbf{(PCy_3)\overline{NiCH_2CH_2CH_2CONH}}$ **(7) and** $\mathbf{(PCy_3)\overline{NiCH_2CH_2CH_2COO}}$ **(8).** A THF (10 cm^3) solution containing 300 mg (1.1 mmol) of $\mathrm{Ni(cod)_2}$, 310 mg (1.1 mmol) of $\mathrm{PCy_3}$, and 94 mg (1.1 mmol) of 3-butenamide was stirred for 24 h at room temperature to obtain a yellow precipitate. The precipitate was collected by filtration, washed with diethyl ether (three times, 10 cm^3 each), and dried under vacuum to yield 130 mg (28%) of **4**. Higher percentage yields seemed to be obtained in large-scale reactions. Complex **8** was prepared analogously by using 210 mg (0.77 mmol) of $\mathrm{Ni(cod)_2}$; yield 110 mg (32%).

$\mathbf{(dppp)\overline{NiCH_2CH(CH_3)CONH}}$ **(5) and** $\mathbf{(dppb)\overline{NiCH_2CH(CH_3)CONH}}$ **(6).** 1,3-Bis(diphenylphosphino)propane (240 mg, 0.58 mmol) was added to a toluene (6 cm^3) solution of **1a** (250 mg, 0.58 mmol). After the reaction mixture was stirred for 12 h at room temperature, the homogeneous yellow solution was condensed to obtain a yellow precipitate, which was separated by filtration, washed with hexane, and recrystallized from acetone. Drying the crystals under vacuum gave yellow **5**; yield 180 mg (56%). Complex **6** was prepared analogously; yield 55%.

$\mathbf{(PCy_3)Pt(methacrylamide)_2}$ **(10) and** $\mathbf{(PCy_3)Pt(}$***N*****-phenylmethacrylamide)$_2$ (11).** Stirring a reaction mixture containing 150 mg (0.37 mmol) of $\mathrm{Pt(cod)_2}$, 120 mg (0.43 mmol) of $\mathrm{PCy_3}$, and 41 mg (0.48 mmol) of methacrylamide in THF (4 cm^3) for 14 h at room temperature gave a white precipitate. The precipitate was washed repeatedly with diethyl ether and THF and dried under vacuum to yield 120 mg (49%) of **10**. Complex **11** was prepared analogously; yield 48%.

$\mathbf{(PCy_3)_2PtH(OCOC(CH_3){=}CH_2)}$ **(12) and** $\mathbf{(PCy_3)_2PtH(OCOCH_2CH{=}CH_2)}$ **(13).** Methacrylic acid (36 μL, 0.43 mmol) was added to a THF (2 cm^3) solution of $\mathrm{Pt(cod)_2}$ (180 mg, 0.43 mmol) and $\mathrm{PCy_3}$ (129 mg, 0.43 mmol) at 0 °C. After the reaction mixture was stirred for 24 h at room temperature, the homogeneous solution was evaporated to dryness. After the white solid was washed with acetone, the remaining solid was crystallized from diethyl ether to obtain white crystals, which were dried under vacuum to yield 120 mg (33%) of **12**. Complex **13** was prepared analogously (**13** is soluble in acetone and was recrystallized from acetone); yield 100 mg (34%).

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[20] One of the possible structures, $[(\mathrm{PEt_3})\overline{\mathrm{NiCH_2C({=}CH_2)CONH}}]_4$, which could not be excluded completely by X-ray analysis alone, is an optically inactive form. In contrast, the present $[(\mathrm{PEt_3})\overline{\mathrm{NiCH_2C^{*}H(CH_3)CONH}}]_4$ structure, which is supported strongly by ^{13}C NMR and X-ray results, has four optically active carbon atoms. Six possible optically different forms are present: *RRRR*, *RRRS*, *RRSS*, *RSRS*, *RSSS*, *SSSS*. Our X-ray results mean only that the 50% *R* and 50% *S* occupancies occur in all the C* positions.

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Reactions of Complexes. A Schlenk tube containing 70 mg (0.17 mmol) of 7 was immersed in an oil bath. After the sample was heated at 210 °C for 3 h, the thermolysis product was analyzed by GLC, which showed formation of 64 mol % of 3-butenamide and 6 mol % of 2-butenamide based on 7. Other reactions listed in Table III were carried out under conditions shown in the table.

Supplementary Material Available: Figure S1, showing the molecular structure of 2, and Tables S1–S3, giving atomic coordinates and equivalent isotropic temperature factors, anisotropic thermal factors, and bond distances and angles (10 pages); Table S4, giving observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

Notes

Photochemical Synthesis and Thermal Interconversion of *mer*- and *fac*-$W(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene)

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Received January 31, 1990

Summary: Both *fac* and *mer* isomers of $W(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene) are formed in a photolysis reaction. They readily interconvert thermally, with the *fac* isomer favored by a ca. 2:1 ratio.

Group 6 pseudooctahedral olefin complexes are an important source of novel coordination stoichiometries and geometries.[1] Several early studies showed a general preference for $M(CO)_4$ derivatives to bind nonconjugated dienes,[2] but we have recently shown that this preference is *inverted* in the case of the $Cr(CO)_3(P(OMe)_3)$ fragment.[3] Our initial speculation was that the inversion was caused by electronic factors; that is, the phosphite adds enough additional electron density to the metal to make the fragment prefer a conjugated diene, which is a superior π-acceptor, instead of a nonconjugated diene, which is a superior σ-donor.[4] However, a single metal ligand environment is insufficient to test this, and we have therefore moved down the triad to tungsten, where steric effects should be minimized and back-bonding emphasized. This paper reports our results, including the photochemical synthesis of both the *mer* and the *fac* isomers of the parent $W(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene) and the determination that the inversion observed with chromium is, in fact, due to *electronic* factors.

Results and Discussion

Irradiation of a pentane solution of $W(CO)_5(P(OMe)_3)$ and 1,5-cyclooctadiene (COD) with the apparatus externally cooled by dry ice produces a mixture of the meridional and facial isomers of tricarbonyl(cyclooctadiene)(trimethyl phosphite)tungsten(0) (eq 1).

$$W(CO)_5(P(OMe)_3) + 1,5\text{-}C_8H_{12} \xrightarrow{h\nu} mer\text{-}W(CO)_3(P(OMe)_3)(\eta^4\text{-}1,5\text{-}C_8H_{12}) + fac\text{-}W(CO)_3(P(OMe)_3)(\eta^4\text{-}1,5\text{-}C_8H_{12}) \quad (1)$$

The components of the reaction mixture are separated by column chromatography on silica with use of a column cooled by a water jacket. Elution with 10:1 pentane–ether is sufficient to separate the two isomers, and a single crystallization renders them spectroscopically pure of minor side products. Final purification of analytically pure materials is accomplished by crystallization of yellow needles from pentane.

The identity of the two isomers is determined by NMR and IR spectroscopy. The *mer* isomer exhibits an NMR spectrum quite similar to that observed for the chromium congener (the sole exception being among the aliphatic hydrogens of cyclooctadiene, where there is greater resolution with Cr, presumably due to the proximity of certain hydrogens to the metal). However, the spectrum of the *fac* isomer contains resonances for the olefinic protons that are much closer together and, more importantly, that show a strong cross peak in a COSY spectrum. This indicates that the protons are in similar, spin-coupled environments and is consistent with the *fac* isomer with the COD ligand asymmetric with respect to a mirror plane *through the C–C double bonds.* In addition, the ^{13}C spectrum of the *mer* complex contains two well-separated resonances, at δ 89.2 and 75.2, assigned to the C=C bonds trans to CO and phosphorus, respectively. For the *fac* complex the olefin resonances are much closer together, at δ 86.3 and 82.4. The infrared spectra of the two complexes are also consistent with the assigned geometry.[5] The *fac* isomer exhibits three strong bands at 1980, 1915, and 1870 cm^{-1}, while localized C_{2v} symmetry in the *mer* isomer yields three bands at 2000 (w), 1920 (s), and 1880 (m) cm^{-1}.

The *fac* geometry was confirmed by a solid-state structural study. Experimental details are provided in Table I, positional and isotropic thermal parameters for

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