

Homogeneous Catalytic Carbonylation of Nitroaromatics. 6. Synthesis and Structure of Two Bis(carbamoyl) Complexes of Ruthenium

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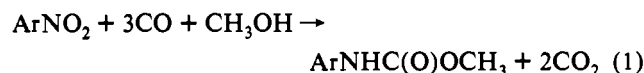
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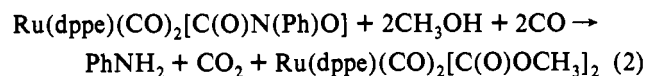
Isopropyl- and benzylamine react with (OC-6-32)-dicarbonylbis(methoxycarbonyl)[1,2-bis(diphenylphosphino)ethane]ruthenium(II), at room temperature by substituting rapidly both of the methoxy groups. The bis(carbamoyl) complex (OC-6-32)-dicarbonylbis(*N*-isopropylcarbamoyl)[1,2-bis(diphenylphosphino)ethane]ruthenium(II) was fully characterized using solution spectroscopy and single-crystal X-ray diffraction [monoclinic crystal system, $P2_1/c$ space group, $a = 9.083(3)$ Å, $b = 22.28(1)$ Å, $c = 19.599(9)$ Å, $\beta = 98.62(3)^\circ$, $V = 3921(10)$ Å³, $Z = 4$]. In addition to the analogous product, the reaction with benzylamine also produced a small amount of crystalline product in which a CO ligand was substituted with benzylamine. This was characterized by single-crystal X-ray diffraction methods as (OC-6-33)-benzylaminecarbonylbis(benzylcarbamoyl)[1,2-bis(diphenylphosphino)ethane]ruthenium(II) [monoclinic crystal system, $P2_1/n$ space group, $a = 15.777(5)$ Å, $b = 16.87(2)$ Å, $c = 16.39(2)$ Å, $\beta = 93.97(6)^\circ$, $V = 4351(10)$ Å³, $Z = 4$].

Introduction

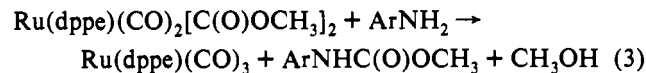
The conversion of nitroaromatics into arylcarbamates (eq 1) occurs at high temperatures under high pressures of CO in the presence of a homogeneous transition metal catalyst, such as



$\text{Ru}(\text{dppe})(\text{CO})_3$ (**1**).¹⁻⁶ The four-member metallocyclic intermediate $\text{Ru}(\text{dppe})(\text{CO})_2[\text{C}(\text{O})\text{N}(\text{Ar})\text{O}]$ (**2**) formed rapidly following the interaction of ArNO_2 with **1** under CO. This species reacted quantitatively with methanol under CO, as shown in eq 2, to generate two isomers of the bis(methoxycarbonyl) complex



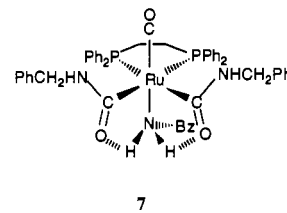
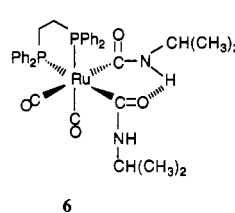
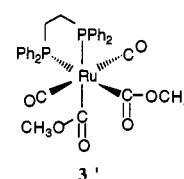
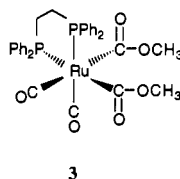
$\text{Ru}(\text{dppe})(\text{CO})_2[\text{C}(\text{O})\text{OCH}_3]_2$ (**3** and **3'**). Earlier work on this system suggested that under catalytic conditions the reaction of **3** with aromatic amines (eq. 3) was the rate-limiting step of the catalysis.⁵



This paper will describe the formation, isolation, and characterization of two bis(carbamoyl) complexes, $\text{Ru}(\text{dppe})(\text{CO})_2[\text{C}(\text{O})\text{NHCH}(\text{CH}_3)_2]_2$ (**6**) and $\text{Ru}(\text{dppe})(\text{CO})(\text{NH}_2\text{Bz})[\text{C}(\text{O})\text{NHCH}(\text{CH}_3)_2]_2$ (**7**), prepared from the reaction of **3** with the corresponding alkyl amines (eq 4). The non consecutive numbering of these structures is used to maintain uniformity between this and the related publications on this subject.^{5,7,8}

$\text{Ru}(\text{dppe})(\text{CO})_2[\text{C}(\text{O})\text{OCH}_3]_2 + 2\text{RNH}_2 \rightarrow \text{Ru}(\text{dppe})(\text{CO})_2[\text{C}(\text{O})\text{NHR}]_2 + 2\text{CH}_3\text{OH} \quad (4)$

being of these structures is used to maintain uniformity between this and the related publications on this subject.^{5,7,8}



Experimental Section

General Procedures. Standard Schlenk techniques were used when working with all organometallic compounds, unless otherwise stated. A nitrogen-filled Vacuum Atmospheres drybox equipped with a Dri-Train Model 40-1 inert gas purifier was employed for manipulations carried out under glovebox conditions. NMR spectroscopy was performed on a Varian-Unity 300 instrument. Infrared spectra were collected on a Mattson Polaris spectrometer. All chemicals were purchased from Aldrich Chemical Co., except $\text{Ru}_3(\text{CO})_{12}$ and dppe (1,2-bis[diphenylphosphino]ethane), which were purchased from Strem Chemical. Solvents were freshly distilled from benzophenone ketyl under nitrogen, except methylene chloride, which was distilled from calcium hydride. Benzyl- and isopropylamine were stored over activated 4 Å sieves prior to use. Ru-

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(8) Gargulak, J. D.; Gladfelter, W. L. *Organometallics*, in press.

* Abstract published in *Advance ACS Abstracts*, December 15, 1993.
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(2) Grate, J. H.; Hamm, D. R.; Valentine, D. H. U. S. Patent 4,603,216, 1986.
(3) Grate, J. H.; Hamm, D. R.; Valentine, D. H. U. S. Patent 4,629,804, 1986.
(4) Grate, J. H.; Hamm, D. R.; Valentine, D. H. U. S. Patent 4,705,883, 1987.
(5) Gargulak, J. D.; Berry, A. J.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1992**, *114*, 8933-8945.
(6) Gargulak, J. D.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1991**, *113*, 1054.

Table 1. Crystallographic Data for Ru(dppe)(CO)₂[C(O)NHCH(CH₃)₂]₂^{1/2}(C₆D₆) (6) and Ru(dppe)(CO)(NH₂Bz)[C(O)NHBz]₂ (7)

	6	7
chem formula	RuC ₃₉ H ₄₃ N ₂ O ₄ P ₂	RuC ₅₀ H ₄₉ N ₃ O ₃ P ₂
fw	766.8	902.97
a, Å	9.083(3)	15.777(5)
b, Å	22.28(1)	16.87(2)
c, Å	19.599(9)	16.39(2)
β, deg	98.62(3)	93.97(6)
V, Å ³	3921(10)	4351(10)
space group	P2 ₁ /c (No. 14)	P2 ₁ /n (No. 14)
Z	4	4
ρ(calcd), g/cm ³	1.299	1.378
temp, °C	-73	-101
λ, Å	0.710 69	0.710 69
μ (cm ⁻¹)	5.1	4.7
transm coeff	0.74–1.21	0.83–1.19
R ^a	0.067	0.065
R _w ^b	0.062	0.065

$$^a R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|. \quad ^b R = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}.$$

(dppe)(CO)₂[C(O)OCH₃]₂ was prepared using the literature procedure⁵ that was refined to allow the isolation of 3 without any detectable 3'.⁸

Preparation of 6. The following procedure was used for the preparation of carbamoyl compounds such as 6 from the reaction of 3 with alkyl amines. A toluene solution (2 mL) of 3 (100 mg, 0.15 mmol) was prepared in a 25-mL Erlenmeyer flask capped with a septum under a nitrogen atmosphere. Isopropylamine (200 μL; 2.4 mmol) was added to this solution. The solution was stirred briefly and allowed to stand at ambient temperature for 1 h. Dry hexanes were added to the solution until it became slightly cloudy. Crystals, formed after the solution was placed in a freezer at -17 °C, were isolated by filtering the solution in air on a coarse glass frit. Yield: >90% by ³¹P NMR spectroscopy, 20–60% isolated. IR (cm⁻¹, toluene): 2029 (s), 1976 (s), 1621 (w, br), 1560 (w, br). ¹H NMR (ppm, C₆D₆): 9.91 (d, J_{HH} = 5.4 Hz, NH), 4.83 (d, J_{HH} = 6.9 Hz, NH), 4.49 (m, CH), 3.73 (m, CH), 3.35 (m, CH), 3.18 (m, CH), 2.43 (m, CH), 1.98 (m, CH), 1.14 (d, J_{HH} = 6.6 Hz, (CH₃)₂), 0.82 (d, J_{HH} = 6.4 Hz, CH₃), 0.74 (d, J_{HH} = 6.3 Hz, CH₃). ³¹P NMR (ppm, C₆D₆): 57.2 (d, J_{PP} = 12.5 Hz), 53.8 (d, J_{PP} = 12.5 Hz). Anal. Calcd for Ru(dppe)(CO)₂[C(O)NHCH(CH₃)₂]₂: C, 59.4; H, 8.8; N, 3.9; P, 8.5. Found: C, 58.85; H, 6.14; N, 3.6; P, 8.41.

X-ray Crystallography of 6^{1/2} (C₆D₆). Colorless prisms were grown from C₆D₆/hexane and one of these was mounted on a glass fiber. Table 1 includes the details of the structural analysis. A preliminary peak search of 24 centered reflections (25° < 2θ < 43°) indicated that the crystal was monoclinic. The space group P2₁/c (No. 14) was uniquely determined based on the systematic absences. During data collection, no decay of intensity was observed in three check reflections measured every 60 min. All non-hydrogen atoms except those in the solvent of crystallization were refined anisotropically. The benzene molecule lies on a center of symmetry and was modeled using a rigid body refinement with multiplicities of the carbon and hydrogen atoms set to 0.5. Most hydrogen atoms were included in the structure factor calculation in idealized positions with d_{C-H} = 0.95 Å and an isotropic temperature factor 20% greater than the B(eq) of the carbon to which they were bonded. The two hydrogens (H11N and H21N) bound to the nitrogens were located and refined using isotropic temperature factors. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.77 and -0.98 e/Å³, respectively. The values of the atomic scattering factors used in the calculations were taken from the usual tabulations, and the effects for anomalous dispersion were included for the non-hydrogen atoms. Selected positional parameters, bond distances, and bond angles are listed in Tables 2–4. Figure 1 shows the molecular structure of 6.

Preparation of 7. In the glovebox a NMR tube was loaded with a solution of 3 (59.4 mM; 0.5 mL of C₆D₆) sealed with a septum and removed from the glovebox. Benzylamine (35 μL, 0.32 mmol) was injected into the tube and allowed to react under ambient conditions. The transformation was monitored after 12 h by ¹H and ³¹P NMR spectroscopy. At this point the concentration of 3 decreased by 80% as determined by ³¹P NMR spectroscopy. Addition of more benzyl amine (40 μL; 0.37 mmol) via the septum resulted in complete disappearance of 3 after several hours. Hexane (0.4 mL) was added to the tube via syringe, and the solution was mixed until it was homogeneous. Additional hexane (1.0

Table 2. Atomic Positional (×10⁴) and Thermal Parameters for Ru(dppe)(CO)₂[C(O)NHCH(CH₃)₂]₂^{1/2}(C₆D₆) (6)

atom	x	y	z	B(eq), Å ²
Ru	3412.7(7)	1991.6(3)	1312.4(3)	1.78(3)
P1	5668(3)	2490(1)	1162(1)	2.1(1)
P2	5070(2)	1367(1)	2060(1)	2.3(1)
O1	1313(8)	2890(3)	506(4)	5.6(4)
O2	3184(7)	1221(3)	5(3)	4.3(3)
O11	4479(6)	2786(3)	2532(2)	3.1(3)
O21	394(6)	1746(3)	1725(3)	3.3(3)
N11	1995(6)	2744(4)	2315(4)	3.7(4)
N21	1480(10)	917(4)	1445(4)	3.4(4)
C1	2090(10)	2559(4)	807(5)	3.5(5)
C2	3380(10)	1495(4)	499(4)	2.7(4)
C11	3340(10)	2578(4)	2195(4)	2.5(4)
C12	1750(10)	3165(5)	2859(6)	4.9(6)
C21	1530(10)	1513(4)	1549(4)	2.2(4)
C23	290(10)	44(5)	1100(6)	6.9(7)
C31	7070(10)	2287(4)	1903(4)	2.8(4)
C41	5870(10)	3294(4)	1135(4)	2.7(4)
C51	6430(10)	2252(4)	386(4)	2.3(4)
C61	4820(10)	1293(4)	2968(4)	2.6(4)
C71	5200(10)	591(4)	1782(4)	2.6(4)
H21N	2100(70)	760(30)	1330(4)	1(2)
H11N	1200(90)	2540(40)	2120(40)	5(3)

Table 3. Selected Bond Distances (Å) for Ru(dppe)(CO)₂[C(O)NHCH(CH₃)₂]₂^{1/2}(C₆D₆) (6)

A. Metal-Ligand Distances			
Ru-P1	2.387(3)	Ru-P2	2.385(2)
Ru-C2	1.937(9)	Ru-C1	1.914(9)
Ru-C21	2.123(9)	Ru-C11	2.176(8)
B. Intraligand Distances			
P1-C31	1.841(8)	P1-C41	1.804(9)
P1-C51	1.844(9)	P2-C32	1.86(1)
P2-C61	1.837(8)	P2-C71	1.823(9)
O1-C1	1.12(1)	O2-C2	1.14(1)
O11-C11	1.23(1)	O21-C21	1.25(1)
N11-C1	1.133(1)	N11-C12	1.46(1)
N21-C21	1.34(1)	N21-C22	1.48(1)

Table 4. Selected Bond Angles (deg) in Ru(dppe)(CO)₂[C(O)NHCH(CH₃)₂]₂^{1/2}(C₆D₆) (6)

A. Ligand-Metal-Ligand			
P1-Ru-P2	82.65(8)	P1-Ru-C1	96.5(3)
P1-Ru-C2	94.2(3)	P1-Ru-C11	86.9(3)
P1-Ru-C21	173.8(2)	P2-Ru-C1	173.0(3)
P2-Ru-C2	96.0(3)	P2-Ru-C11	87.3(2)
P2-Ru-C21	91.6(2)	C1-Ru-C2	91.0(4)
C1-Ru-C11	85.7(4)	C1-Ru-C21	88.9(4)
C2-Ru-C11	176.7(3)	C2-Ru-C21	88.7(3)
C11-Ru-C21	90.5(3)		
B. Ligands			
C11-N11-C12	123.5(8)	C21-N21-C22	125.7(8)
Ru-C1-O1	179.6(9)	Ru-C2-O2	172.1(7)
Ru-C11-O11	122.2(7)	Ru-C11-N11	116.3(6)
O11-C11-N11	121.2(8)	N11-C12-C13	111(1)
N11-C12-C14	111(1)	Ru-P2-C32	109.1(3)
Ru-C21-O21	125.3(6)	Ru-C21-N21	118.2(7)
O21-C21-N21	116.2(8)	N21-C22-C23	109.8(9)
Ru-P1-C31	107.2(3)	Ru-P1-C41	123.9(3)
Ru-P1-C51	113.9(3)	Ru-P2-C61	119.2(3)
Ru-P2-C71	115.7(3)	N21-C22-C24	111.9(8)

mL) was added to the tube carefully so the solvents layered. Crystals formed at the interface as the two solvents interdiffused, giving an isolated yield of 7%. ¹H NMR (ppm, C₆D₆): 6.55 (t, J_{HH} = 4.1 Hz, NH₂), 6.04 (m, b, NH), 5.0 (m, b, NH), 4.75 (d, J_{HH} = 12.9 Hz, CH₂), 4.51 (d, J_{HH} = 12.9 Hz, CH₂), 2.75 (m, CH₂CH₂), 2.2 (s, CH₂). ³¹P NMR (ppm, C₆D₆): 43.5(s). Anal. Calcd for Ru(dppe)(CO)(NH₂CH₂Ph)-[C(O)NHCH₂Ph]₂: C, 66.5; H, 5.5; N, 4.7; P, 6.8. Found: C, 65.2; H, 4.9; N, 4.5; P, 7.0.

X-ray Crystallography of 7. Colorless plates were grown from a mixture of benzene and hexane, and one of these was mounted on a glass fiber. Table 1 includes the details of the structural analysis. A preliminary

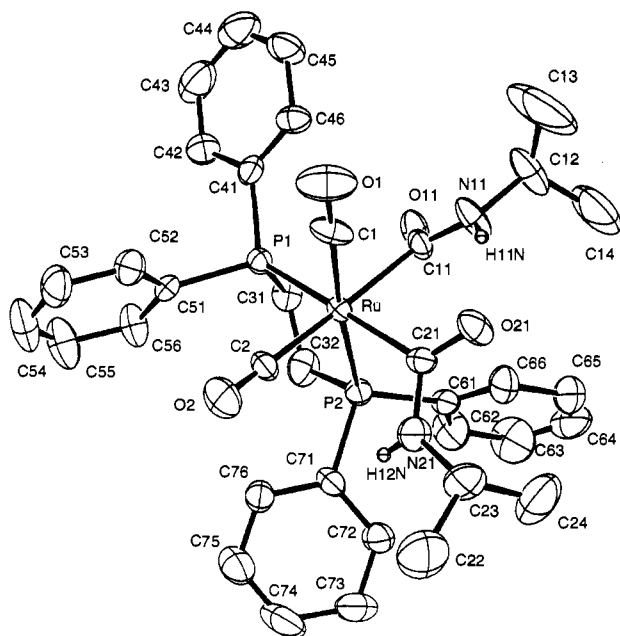


Figure 1. Molecular structure and atom labeling of $\text{Ru}(\text{dppe})(\text{CO})_2\text{-}[\text{C}(\text{O})\text{NHCH}(\text{CH}_3)_2]_2$ (**6**) with thermal ellipsoids shown at the 50% level.

Table 5. Atomic Positional ($\times 10^4$) and Thermal Parameters for $\text{Ru}(\text{dppe})(\text{CO})(\text{NH}_2\text{Bz})[\text{C}(\text{O})\text{NHBz}]_2$ (**7**)

atom	x	y	z	$B(\text{eq}), \text{\AA}^2$
Ru	2979.6(4)	1652.8(4)	1948.6(4)	1.60(2)
P1	3688(1)	766(1)	2904(1)	1.88(9)
P2	1917(1)	644(1)	1856(1)	1.97(9)
O3	3766(4)	885(4)	0537(4)	3.3(3)
O51	3873(3)	3145(3)	2486(4)	2.6(3)
O61	1721(4)	2911(3)	1472(4)	3.1(3)
N51	4548(4)	2544(4)	1526(5)	2.7(3)
N61	2503(4)	2655(4)	441(5)	2.9(3)
N71	2429(4)	2324(4)	2927(4)	2.5(3)
C1	2929(5)	-10(5)	3123(5)	2.4(4)
C2	2406(5)	-237(5)	2357(6)	2.4(4)
C3	3449(5)	1184(4)	1088(5)	2.0(3)
C11	4102(5)	1095(5)	3905(5)	2.0(3)
C21	4616(5)	237(5)	2546(5)	2.2(4)
C31	0900(5)	803(5)	2291(5)	2.1(3)
C41	1544(5)	242(5)	862(5)	2.4(4)
C51	3900(5)	2557(5)	2025(5)	2.0(3)
C52	5182(5)	3159(5)	1450(6)	3.1(4)
C53	6009(5)	2964(5)	1900(6)	2.5(4)
C61	2293(5)	2504(5)	1234(5)	2.2(4)
C62	2103(6)	3269(6)	-87(5)	3.4(4)
C63	2616(5)	4007(5)	-207(5)	2.7(4)

peak search of 23 centered reflections ($19^\circ < 2\theta < 33^\circ$) indicated that the crystal was monoclinic. The space group $P2_1/n$ (No. 14) was uniquely determined based on the systematic absences. During data collection, no decay of intensity was observed in three check reflections measured every 60 min. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculation in idealized positions with $d_{\text{C-H}} = 0.95 \text{ \AA}$ and an isotropic temperature factor 20% greater than the $B(\text{eq})$ of the carbon to which they were bonded. The maximum and minimum peaks on the final difference Fourier map corresponded to $+0.92$ and -0.72 e/\AA^3 , respectively. The values of the atomic scattering factors used in the calculations were taken from the usual tabulations, and the effects for anomalous dispersion were included for the non-hydrogen atoms. Selected positional parameters, bond distances, and bond angles are listed in Tables 5–7. Figure 2 shows the molecular structure of **7**.

Results

Formation, Characterization, and Structure of 6. Addition of excess isopropylamine to a solution of **3** in benzene (or toluene) resulted in complete disappearance of **3** within 5 min. After 1

Table 6. Selected Bond Distances (\AA) in $\text{Ru}(\text{dppe})(\text{CO})(\text{NH}_2\text{Bz})[\text{C}(\text{O})\text{NHBz}]_2$ (**7**)

A. Metal-Ligand Distances			
Ru1-P1	2.386(3)	Ru1-C61	2.105(8)
Ru1-P2	2.386(2)	Ru1-C51	2.104(8)
Ru1-N71	2.192(7)	Ru1-C3	1.819(8)
B. Intraligand Distances			
P1-C1	1.827(8)	P1-C11	1.812(8)
P1-C21	1.845(8)	P2-C2	1.841(8)
P2-C31	1.820(8)	P2-C41	1.825(9)
O3-C3	1.176(9)	O51-C51	1.249(9)
O61-C61	1.220(9)	N51-C51	1.35(1)
N51-C52	1.45(1)	N61-C61	1.39(1)
N61-C62	1.46(1)	N71-C71	1.46(1)
C52-C53	1.49(1)	C1-C2	1.50(1)
C62-C63	1.51(1)	C71-C72	1.54(1)

Table 7. Selected Bond Angles (deg) in $\text{Ru}(\text{dppe})(\text{CO})(\text{NH}_2\text{Bz})[\text{C}(\text{O})\text{NHBz}]_2$ (**7**)

A. Ligand-Metal-Ligand			
P1-Ru1-P2	83.66(9)	P2-Ru1-C61	96.8(2)
P1-Ru1-N71	92.0(2)	P2-Ru1-C51	179.0(2)
P1-Ru1-C3	92.2(3)	P2-Ru1-C3	87.9(2)
P1-Ru1-C51	97.2(2)	P2-Ru1-N71	95.9(2)
P1-Ru1-C61	172.8(2)	N71-Ru1-C3	174.6(3)
C3-Ru1-C51	92.5(3)	N71-Ru1-C51	83.6(3)
N71-Ru1-C61	80.8(3)	C3-Ru1-C61	95.0(3)
C51-Ru1-C61	82.3(3)		
B. Ligands			
Ru1-C3-O3	178.9(7)	C61-N61-C62	124.3(7)
Ru1-N71-C71	127.6(5)	C51-N51-C52	126.4(7)
Ru1-P1-C1	107.2(3)	N51-C52-C53	112.7(7)
Ru1-P1-C11	121.7(3)	O51-C51-N51	116.0(7)
Ru1-P1-C21	116.1(3)	N61-C62-C63	116.6(7)
Ru1-P2-C2	106.0(3)	N71-C71-C72	112.5(7)
Ru1-P2-C31	120.3(3)	O61-C61-N61	115.3(8)
Ru1-P2-C41	120.2(3)	Ru1-C61-O61	124.7(6)
Ru1-C61-N61	120.0(6)	Ru1-C51-N51	120.0(6)
Ru1-C51-O51	123.9(6)		

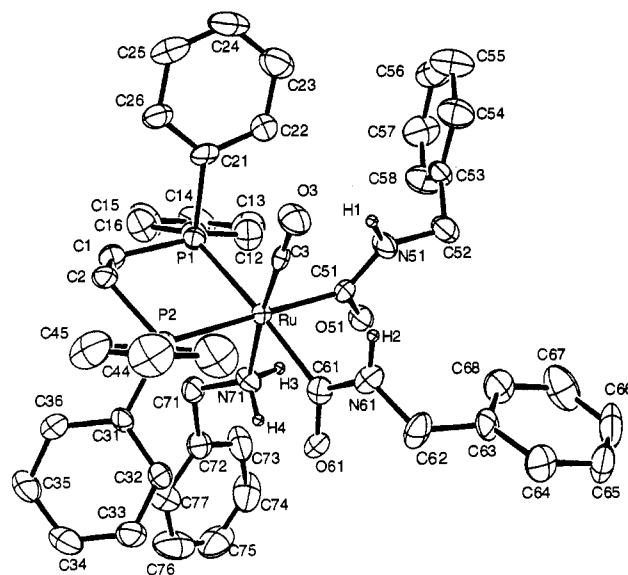


Figure 2. Molecular structure and atom labeling of $\text{Ru}(\text{dppe})(\text{CO})(\text{NH}_2\text{Bz})[\text{C}(\text{O})\text{NHBz}]_2$ (**7**) with thermal ellipsoids shown at the 50% level.

h two predominant resonances are observed in the ^{31}P NMR spectrum at 57.2 (d, $J_{\text{PP}} = 12.5 \text{ Hz}$) and 53.8 (d, $J_{\text{PP}} = 12.5 \text{ Hz}$) ppm, due to **6**. These resonances account for approximately 90% of the intensity. Equation 4 illustrates the reaction that leads to the high-yield preparation of **6**. The synthesis and crystallization of **6** can be carried out under atmospheric conditions with no effect on the yield. The compound was stored under nitrogen,

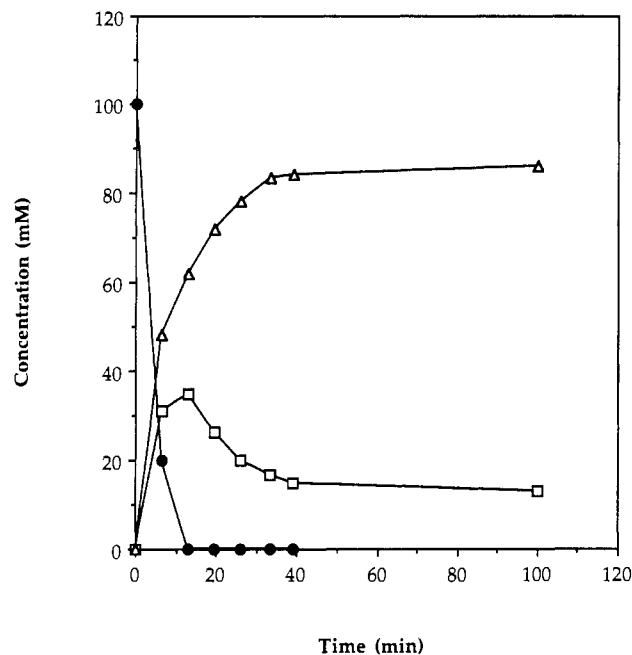


Figure 3. Concentration profile for the reaction of **3** and **3'** with excess isopropylamine: (●) **3** and **3'**; (□) **8** or **9**; (Δ) **6**. [**3**] = 0.030 M; [*i*-prNH₂] = 2 M.

however, because slow decomposition results with exposure to air over several weeks.

The mass spectral and elemental analytical data of the crystalline product established that 2 equiv of nitrogen were added to the metal and that four carbonyl units were present on the compound. The ¹H NMR spectrum of the reaction mixture at completion also showed that 2 equiv of methanol were liberated during formation of the new species. The solution spectroscopic data were consistent with the structure obtained in the solid state. Of particular interest was the observation that the two amide protons were separated by 5 ppm. This indicated that the intramolecular hydrogen bond observed in the solid (discussed below) was present in solution. The hydrogen-bonded proton is assigned as the amide proton with the downfield chemical shift in the ¹H NMR spectrum (d, 9.91 ppm) compared to the non-hydrogen-bonded amide proton (d, 4.49 ppm).

While monitoring the transformation of **3** to **6** using ³¹P NMR spectroscopy, a singlet in the spectrum (41.9 ppm) attributed to a symmetric species was observed at the beginning of the reaction, but gradually decreased in intensity as the resonances due to **6** appeared. Figure 3 shows the concentration profile for the species involved in this reaction. Although a small amount (13%) of the singlet remained at the end of the reaction, none was observed following crystallization. Dissolving crystalline **6** in benzene and addition of CH₃OH (5 M) result in approximately 80% conversion of **6** back to **3** over 12 h, showing the amination to be reversible. The other products (20%) of the methanolysis were unidentified.

The solid-state structure of **6** (Figure 1) has features typical for octahedral ruthenium(II) carbonyl complexes. The plane containing O11, C11, N11, and H11N (maximum out of plane deviation = 0.0372 Å) and the plane containing O21, C21, N21, and H21N (maximum out of plane deviation = 0.025 Å) are locked into a six member ring by the hydrogen-bonded amide proton H11N, whose position and isotropic thermal parameters were refined in the final solution. The two planes intersect the plane comprised of C11–Ru–C21 at a dihedral angle of 43.4°. The hydrogen bond formed between H11N and O21 has a bond distance of 2.032(6) Å, and has an N11–H11N–O21 bond angle of 148.4(7)°.

Formation, Characterization, and Structure of 7. Twelve hours after the addition of an 8-fold excess of benzylamine to a 60 mM

solution of **3** in C₆D₆, a mixture of four metal phosphine complexes were noted as separate signals in the ³¹P NMR spectrum. Approximately 20% of the material was **3** and **3'** (d, 52.2 ppm; 45.9 ppm; *J*_{PP} = 12.5 Hz; s, 43.6 ppm) and 5% was Ru(dppe)(CO)-(NH₂Bz)[C(O)NHCH₂Ph]₂ (**7**) (s, 43.5 ppm). The major component of the solution (60% of the material) was Ru(dppe)-(CO)₂[C(O)NHCH₂Ph]₂, the benzyl analog of **6** (d, 57.1 ppm; d, 53.6 ppm; *J*_{PP} = 12.4 Hz). This assignment is based on the similarity of chemical shifts to **6** in the ³¹P NMR spectrum and the expected similarity in reactivity to that found between **3** and isopropylamine. An additional set of peaks (d, 57.0 ppm; d, 52.7 ppm; *J*_{PP} = 12.4 Hz) were unidentified.

An additional 40 μL of PhCH₂NH₂ brought the total concentration to 1.1 M (18-fold excess) and resulted in the nearly complete consumption of **3** (3% remained). The rest of the mixture consisted of Ru(dppe)(CO)₂[C(O)NHCH₂Ph]₂ (75%), an unidentified material (s, 41.7 ppm; 12%), and **7** (7%). Small amounts (<2%) of other unidentified materials were also present. After layering hexane over the aromatic solvent, crystals of **7** formed within 2 days. These crystals were kept in solution at -14 °C until their removal for low-temperature X-ray analysis.

Elemental analysis and mass spectrometry established that three amines and three CO units were present in the complex. The ¹H NMR spectrum of the isolated solid, dissolved in C₆D₆, was consistent with the solid-state structure described below and showed no downfield resonance characteristic of the hydrogen-bonded amide proton of **6**. A broad singlet was located at 6.55 ppm, which can be attributed to the protons on the amine. A broad triplet was observed at 6.04 ppm due to one carbamoyl proton, and a broad resonance at 5.0 ppm was due to the other. Two doublets were observed at 4.75 and 4.51 ppm and can be attributed to the benzylic protons on the two carbamoyl moieties, with a coupling of 13 Hz observed to the carbamoyl hydrogen. A broad resonance at 2.75 ppm was due to the four protons of the ethylene backbone of the phosphine ligand. The benzylic protons of the amine ligand were observed at 2.2 ppm as a broad singlet. Resonances from the phosphine ligand are also present in the aromatic region. A singlet at 43.5 ppm is the only signal observed in the ³¹P NMR spectrum.

The structure of **7** is illustrated in Figure 2. The Ru–N71 bond length is typical for coordination of an amine to an octahedral Ru(II). The orientation of the amine is such that the protons are directed toward the two carbamoyl oxygens forming hydrogen bonds locking the carbamoyl nitrogens above the P–Ru–P plane. The heteroatom interactions of the hydrogen-bonded N–O atoms are similar in magnitude to those found in **6**, with values for N71–O61 and N71–O51 of 2.746(7) and 2.803(8) Å, respectively. The bidentate phosphine ligand remains structurally similar to those in other (dppe)Ru²⁺ compounds we have presented, with Ru–P1 and Ru–P2 bond lengths of 2.386(3) Å. The Ru–C3 carbonyl bond length (1.819(8) Å) is approximately 0.1 Å shorter than that for the metal carbonyl of **6**.

Discussion

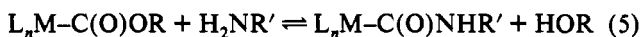
Numerous examples of structurally characterized η¹-mono-carbamoyl transition metal complexes are known,^{9–14} however, only one other bis(carbamoyl) complex, Hg[C(O)NEt₂]₂, has been structurally characterized.¹⁴ The syntheses described here are based on the substitution reaction shown in eq 5, which has

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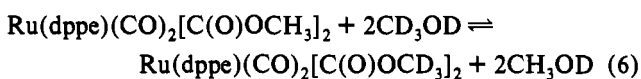
Table 8. Selected Bond Distances (Å) and Angles (deg) η^1 -Carbamoyl Compounds

compound	M-C	C-N	C-O	M-C-N	M-C-O	O-C-N	ref
Pt(PPh ₃) ₂ [C(O)Ph][C(O)NEt ₂]	2.02(1)	1.41(2)	1.23(2)	118.6(8)	123.4(1)	117.7(1)	9
Hg[C(O)NEt ₂] ₂	2.13(2)	1.34(6)	1.24(6)				14
Mn(CO) ₄ (NH ₂ CH ₃)[C(O)NHCH ₃]	2.11(1)	1.44(3)	1.22(2)	123(1)	120(2)	117(2)	12
Ni(PEt ₃) ₂ [C(O)NEt ₂]I	1.882(7)	1.359(7)	1.237(4)	121(1)	119.6(4)	120.7(4)	13
W(η^5 -C ₅ H ₅)(CO) ₂ (NH ₂ CH ₃)[C(O)NHCH ₃]	2.25(3)	1.37(3)	1.25(3)	118(2)	125(2)	117(2)	10
Ru(dppe)(CO) ₂ [C(O)NHCH(CH ₃) ₂] ₂	2.176(8)	1.33(1)	1.23(1)	116.3(6)	122.2(7)	121.2(8)	this work
Ru(dppe)(CO)(NH ₂ Bz)[C(O)NHBz] ₂	2.123(9)	1.34(1)	1.25(1)	118.2(7)	125.3(6)	116.2(8)	this work
	2.105(8)	1.35(1)	1.249(9)	120(6)	123.9(6)	116.0(7)	
	2.104(8)	1.39(1)	1.220(9)	120(6)	124.7(6)	115.3(8)	

been observed for several alkoxy carbonyl complexes.^{15,16} The



analogous substitution among organic esters requires acid or base catalysis and elevated temperatures. Understanding the accelerating effect of the metal complex requires knowledge of the mechanism of this reaction. For complexes which do not contain any other CO ligands, there are three reasonable starting points for the mechanism of this reaction: (a) $L_nMC(O)-OR$ dissociation into ionic intermediates, (b) migratory deinsertion of the OR group following formation of a vacant site, and (c) direct nucleophilic attack on the ester carbonyl. Metal complexes which also contain ancillary CO ligands, as does **3**, offer a fourth possibility: (d) direct nucleophilic attack on a metal carbonyl ligand followed by dissociation of the alcohol (or alkoxide). In separate kinetic and mechanistic studies of the transesterification of **3** (eq 6), we were able to rule out mechanisms a and b.⁸ Because



the first steps of mechanisms a and b in both the transesterification and the amination reactions are independent of the entering nucleophile, we can, by analogy, rule out a and b as mechanisms of the amination. Our results do not allow the discrimination between attack at the methoxycarbonyl or at the metal carbonyl.

During the reaction between **3** and isopropyl amine, an unidentified species forms rapidly and then disappears as **6** appears (Figure 3). Although we do not have enough spectroscopic evidence to characterize this compound, we speculate that it is either the monosubstituted complex, $Ru(dppe)(CO)_2[C(O)OMe]-[C(O)NHCH(CH_3)_2]$ (**8**) or the symmetric isomer of the disubstituted complex $Ru(dppe)(CO)_2[C(O)NHCH(CH_3)_2]_2$ (**9**).

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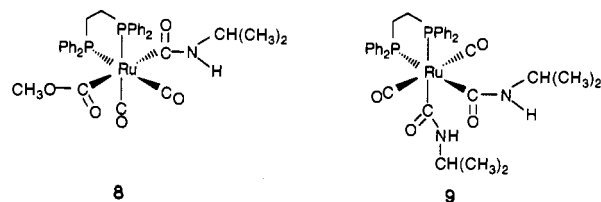
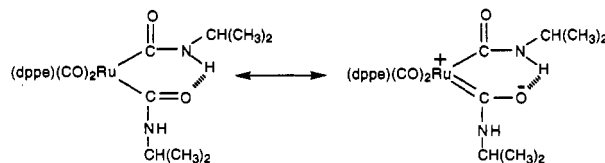


Table 8 compares the structures of **6** and **7** to those of known η^1 -carbamoyl complexes. The most interesting comparison, however, is between the Ru-C11 (2.176(8) Å) and Ru-C21 (2.123(9) Å) bonds of **6**. The notable lengthening of one of the Ru-C bonds could be due to a trans influence caused by differences in the phosphine (P1) and the metal carbonyl (C2). In addition, the presence of the H-bond may increase the importance of the structure of the carbenoid resonance hybrid shown below. These resonance structures emphasize the relationship of **6** to metalla- β -diketones and their derivatives.¹⁷ The C-O [C11-O11 = 1.23(1) Å; C21-O21 = 1.25(1) Å] and C-N [C11-N11 = 1.33(1) Å; C21-N21 = 1.34(1) Å] bond lengths of the carbamoyl ligands on **6** are not significantly different.



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Supplementary Material Available: Tables of crystallographic data, complete atom positions, bond distances and angles, and thermal parameters (33 pages). Ordering information is given on any current masthead page.

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