

# X-ray Crystal Structure Determination of (Ph<sub>4</sub>C<sub>4</sub>CO)(CO)<sub>2</sub>Ru(NHEt<sub>2</sub>): A Reactive Catalytic Intermediate in Transalkylation of Amines

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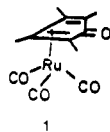
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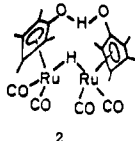
Reaction of (Ph<sub>4</sub>C<sub>4</sub>CO)(CO)<sub>3</sub>Ru with diethylamine in a toluene-water mixture at room temperature affords the complex (Ph<sub>4</sub>C<sub>4</sub>CO)(CO)<sub>2</sub>Ru(NHEt<sub>2</sub>) (3). Its structure was determined by X-ray diffraction analysis and found to possess a pseudotetrahedral geometry [monoclinic; *a* = 10.386 (2) Å, *b* = 19.953 (3) Å, *c* = 14.664 (7) Å; β = 103.07 (4)°; *V* = 2960.1 Å<sup>3</sup>; *Z* = 4; *D*<sub>calc</sub> = 1.379 g·cm<sup>-3</sup>; *F*(000) = 1264; space group *P*2<sub>1</sub>/*c*; *S* (goodness-of-fit) = 1.31 e; *R* = 0.042 (3604 reflections; *I* > 3σ<sub>*I*</sub>)]. The cyclopentadienone (CPD) ligand is found in a η<sup>4</sup> coordination, and its carbonyl is twisted by 6° from the ring plane. Its oxygen atom and the ruthenium coordinated nitrogen atom are hydrogen bonded (NH...O) with O...N and O...H distances of 2.848 and 1.98 Å, respectively. The H atom (N-H) was unambiguously located in the difference Fourier map. Experimental evidence indicates that the NH...O hydrogen bond is the major contributing factor to the thermodynamic stability of this type of coordinated amine complexes. A comparison of structural parameters and spectral data of 3 with two other structurally related complexes is included.

## Introduction

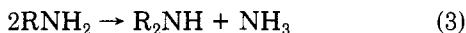
Ruthenium carbonyl cyclopentadienone (CPD) complexes exhibit a broad and interesting spectrum of catalytic activity with a variety of organic substrates.<sup>1-4</sup> Catalytic transalkylation of amines is an interesting and potentially valuable method for the synthesis of unsymmetrical amines.<sup>5-8</sup> In a recent report we have described a catalytic reaction of ruthenium carbonyl cyclopentadienone complexes with primary, secondary, and tertiary amines.<sup>9</sup> It was found that 1 as well as 2, in the presence of water,



CPD phenyls were omitted for clarity.



induces cleavage of carbon-nitrogen bonds in amines. The molecular fragments of this reaction are an aldehyde and an amine bearing one less alkyl group. Being a reversible reaction, the net outcome of the catalytic process with two structurally different tertiary amines is transalkylation (eq 1). With primary or secondary amines disproportionation takes place (eq 2 and 3).



Efforts were directed toward the understanding of the mechanism of these reactions. Thus, stoichiometric reactions between complex 1 and various amines under relatively mild conditions led to the isolation of amine

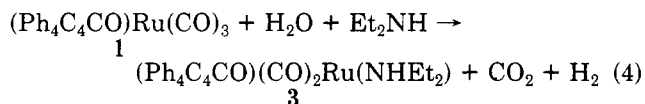
bearing complexes.<sup>9</sup> Most interesting is the fact that tertiary and secondary amines (of the same structural type) yield an identical complex that carries a secondary amine ligand (vide infra). It was established that these amine bearing complexes participate in the catalytic cycles of transalkylation and disproportionation reactions (eq 1-3).

On the basis of spectroscopic and elemental analyses we have assigned a general molecular formula (Ph<sub>4</sub>C<sub>4</sub>C=O)(CO)<sub>2</sub>Ru(NHRR') (R' = R or H) to these aliphatic amine complexes. While primary and secondary amines generate stable complexes, Me<sub>3</sub>N is hitherto the only tertiary amine that gave an unstable but isolable complex.<sup>9</sup>

Adams et al.<sup>10</sup> have isolated and characterized an amino-carbene osmium complex from the reaction of an osmium cluster with trimethylamine. It was found that this complex catalyzes transalkylation of amines, and a mechanism was proposed.<sup>10</sup> A carbene intermediate has also been considered by Laine et al. in the Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed transalkylation of amines.<sup>11</sup>

## Results and Discussion

Catalytically reactive organometallic intermediates usually carry important mechanistic information. Their isolation and characterization are therefore highly important in mechanism studies of catalytic processes. Since a series of isostructural complexes was prepared by using reactions 1 and 2 with various amines, an unambiguous structural characterization was found necessary. For this purpose we have now prepared dicarbonyl(diethylamine)(tetraphenylcyclopentadienone)ruthenium (3). It was obtained as an air-stable complex by reacting 1 and diethylamine in the presence of water at room temperature (eq 4), followed by chromatographic purification and



crystallization (see Experimental Section). It is noteworthy that the same complex 3 was also isolated when tri-

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**Table I. Atomic Positional and Thermal Parameters of Compound 3**

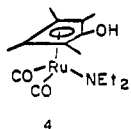
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}, \text{\AA}^2$
Ru(1)	0.3559 (1)	0.1792 (1)	0.7410 (1)	0.0299 (1)
C(2)	0.2414 (6)	0.1154 (3)	0.7739 (4)	0.0503 (15)
O(3)	0.1655 (4)	0.0794 (2)	0.7912 (3)	0.0822 (14)
C(4)	0.3667 (5)	0.2196 (3)	0.8571 (3)	0.0463 (13)
O(5)	0.3673 (5)	0.2446 (2)	0.9267 (3)	0.0887 (14)
C(6)	0.4539 (4)	0.1962 (2)	0.6082 (3)	0.0286 (12)
C(7)	0.4310 (4)	0.2581 (2)	0.6571 (3)	0.0291 (12)
C(8)	0.2911 (4)	0.2652 (2)	0.6486 (3)	0.0288 (12)
C(9)	0.2279 (4)	0.2059 (2)	0.6049 (3)	0.0297 (13)
C(10)	0.3267 (4)	0.1609 (2)	0.5871 (3)	0.0269 (13)
O(11)	0.5632 (3)	0.1739 (2)	0.6006 (2)	0.0383 (9)
C(12)	0.5315 (4)	0.3106 (2)	0.6876 (3)	0.0320 (13)
C(13)	0.6265 (5)	0.3221 (3)	0.6369 (4)	0.0454 (14)
C(14)	0.7210 (5)	0.3719 (3)	0.6645 (5)	0.0612 (15)
C(15)	0.7213 (6)	0.4105 (3)	0.7412 (5)	0.0600 (15)
C(16)	0.6281 (6)	0.3998 (3)	0.7917 (4)	0.0542 (15)
C(17)	0.5317 (5)	0.3506 (2)	0.7660 (4)	0.0408 (14)
C(18)	0.2188 (4)	0.3282 (2)	0.6577 (3)	0.0355 (12)
C(19)	0.1687 (6)	0.3447 (3)	0.7336 (4)	0.0584 (15)
C(20)	0.1018 (6)	0.4042 (3)	0.7358 (5)	0.0766 (17)
C(21)	0.0823 (6)	0.4470 (3)	0.6635 (6)	0.0799 (15)
C(22)	0.1331 (8)	0.4318 (3)	0.5875 (6)	0.0967 (19)
C(23)	0.2024 (7)	0.3727 (3)	0.5849 (5)	0.0669 (16)
C(24)	0.0827 (4)	0.1996 (2)	0.5690 (3)	0.0321 (12)
C(25)	-0.0054 (5)	0.2031 (3)	0.6266 (4)	0.0439 (13)
C(26)	-0.1403 (5)	0.2002 (3)	0.5889 (5)	0.0555 (15)
C(27)	-0.1856 (5)	0.1954 (3)	0.4945 (5)	0.0589 (15)
C(28)	-0.1003 (5)	0.1924 (3)	0.4362 (4)	0.0542 (15)
C(29)	0.0357 (5)	0.1946 (3)	0.4736 (4)	0.0447 (13)
C(30)	0.3033 (4)	0.0967 (2)	0.5365 (3)	0.0302 (12)
C(31)	0.2049 (5)	0.0522 (2)	0.5480 (3)	0.0408 (14)
C(32)	0.1835 (5)	-0.0070 (2)	0.4978 (4)	0.0496 (14)
C(33)	0.2590 (6)	-0.0220 (3)	0.4350 (4)	0.0606 (16)
C(34)	0.3558 (6)	0.0210 (3)	0.4222 (4)	0.0639 (15)
C(35)	0.3776 (5)	0.0799 (2)	0.4727 (3)	0.0431 (14)
N(36)	0.5460 (4)	0.1246 (2)	0.7795 (3)	0.0386 (12)
C(37)	0.5400 (6)	0.0524 (3)	0.8015 (4)	0.0534 (15)
C(38)	0.5188 (7)	0.0383 (4)	0.8965 (5)	0.0839 (17)
C(39)	0.6519 (6)	0.1618 (3)	0.8454 (4)	0.0623 (15)
C(40)	0.7887 (6)	0.1326 (3)	0.8539 (5)	0.0887 (17)
H(36)	0.572 (2)	0.128 (2)	0.722 (2)	0.050 (2)

<sup>a</sup>  $U_{eq}$  is one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

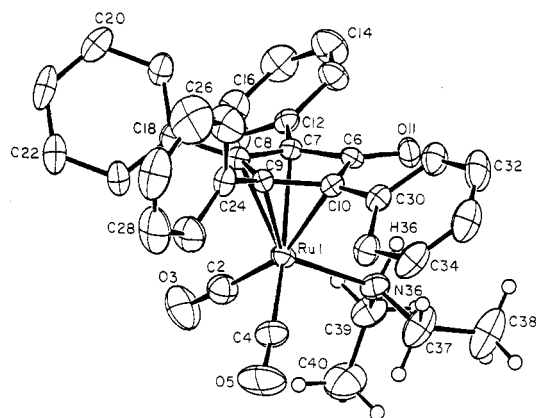
ethylamine and 1 were subjected to catalysis conditions, i.e., 140 °C.

The complete X-ray structure of 3 is presented in Figure 1. Atomic coordinates are listed in Table I, and selected bond distances and angles are summarized in Table II. Structure 3 represents a  $d^8$ , 18e complex with a pseudotetrahedral geometry. The CPD ring is almost planar with its carbonyl twisted by 6° from the ring plane, and it is essentially in a  $\eta^4$  coordination; the distance Ru-C(6) (2.417 Å) is substantially longer than the distance of the other four ring carbon atoms to Ru (2.199–2.246 Å).

An interesting feature of the present structure is the hydrogen-bonded system NH(36)···O(11), 2.848 Å, with an N(36)–H(36)···O(11) angle of 150°. The H(36) atom was clearly located in a difference Fourier map. Although its position could not be determined precisely from the X-ray data, the observed N(36)–H(36) bond length of 0.96 (3) Å vs 1.98 Å for H(36)···O(11) clearly points to a nitrogen rather than an oxygen bound H atom (N–H···O). These results rule out the alternative isomeric  $d^6$  structure 4 with



$\eta^5$ -CPD ligand as well as an amino-carbene structure (vide supra). On steric grounds, the lowest energy conformation

**Figure 1.** An ORTEP diagram of 3 (40% probability ellipsoids are shown).**Table II. Selected Bond Distances and Bond Angles**

Bond Distances (Å)			
Ru(1)–C(2)	1.879 (6)	C(6)–C(7)	1.472 (6)
Ru(1)–C(4)	1.862 (4)	C(6)–C(10)	1.467 (5)
Ru(1)–C(6)	2.417 (4)	C(6)–O(11)	1.247 (5)
Ru(1)–C(7)	2.246 (4)	C(7)–C(8)	1.437 (5)
Ru(1)–C(8)	2.199 (4)	C(8)–C(9)	1.431 (5)
Ru(1)–C(9)	2.200 (4)	C(9)–C(10)	1.431 (6)
Ru(1)–C(10)	2.237 (4)	N(36)–C(37)	1.482 (7)
Ru(1)–N(36)	2.214 (4)	N(36)–C(39)	1.486 (6)
C(2)–O(3)	1.137 (7)	C(37)–C(38)	1.486 (9)
C(4)–O(5)	1.133 (6)	C(39)–C(40)	1.515 (8)

Bond Angles (deg)			
C(10)–Ru(1)–N(36)	95.0 (2)	C(2)–Ru(1)–C(4)	88.2 (2)
C(9)–Ru(1)–N(36)	132.3 (2)	Ru(1)–C(2)–O(3)	175.6 (5)
C(9)–Ru(1)–C(10)	37.6 (2)	Ru(1)–C(4)–O(5)	176.9 (5)
C(8)–Ru(1)–N(36)	132.3 (2)	Ru(1)–C(6)–O(11)	125.4 (3)
C(8)–Ru(1)–C(10)	63.3 (2)	Ru(1)–C(6)–C(10)	65.1 (2)
C(8)–Ru(1)–C(9)	38.0 (2)	Ru(1)–C(6)–C(7)	65.4 (2)
C(7)–Ru(1)–N(36)	94.9 (2)	C(10)–C(6)–O(11)	127.2 (4)
C(7)–Ru(1)–C(10)	62.9 (2)	C(7)–C(6)–O(11)	126.3 (4)
C(7)–Ru(1)–C(9)	62.9 (2)	C(7)–C(6)–C(10)	105.5 (4)
C(7)–Ru(1)–C(8)	37.7 (2)	Ru(1)–C(7)–C(6)	78.0 (2)
C(6)–Ru(1)–N(36)	76.2 (2)	C(6)–C(7)–C(8)	108.2 (4)
C(6)–Ru(1)–C(10)	36.5 (2)	Ru(1)–C(7)–C(8)	69.4 (2)
C(6)–Ru(1)–C(9)	60.8 (2)	Ru(1)–C(8)–C(7)	72.9 (2)
C(6)–Ru(1)–C(8)	61.2 (2)	C(7)–C(8)–C(9)	108.0 (4)
C(6)–Ru(1)–C(7)	36.6 (1)	Ru(1)–C(8)–C(9)	71.1 (2)
C(4)–Ru(1)–N(36)	96.5 (2)	Ru(1)–C(9)–C(8)	71.0 (2)
C(4)–Ru(1)–C(10)	163.3 (2)	C(8)–C(9)–C(10)	108.9 (4)
C(4)–Ru(1)–C(9)	128.6 (2)	Ru(1)–C(9)–C(10)	72.6 (3)
C(4)–Ru(1)–C(8)	100.0 (2)	C(6)–C(10)–C(9)	108.0 (4)
C(4)–Ru(1)–C(7)	104.0 (2)	Ru(1)–C(10)–C(9)	69.8 (2)
C(4)–Ru(1)–C(6)	136.5 (2)	Ru(1)–C(10)–C(6)	78.5 (3)
C(2)–Ru(1)–N(36)	100.4 (2)	Ru(1)–N(36)–C(39)	114.0 (3)
C(2)–Ru(1)–C(10)	101.6 (2)	Ru(1)–N(36)–C(37)	117.1 (4)
C(2)–Ru(1)–C(9)	96.4 (2)	C(37)–N(36)–C(39)	113.8 (4)
C(2)–Ru(1)–C(8)	124.4 (2)	N(36)–C(37)–C(38)	114.4 (5)
C(2)–Ru(1)–C(7)	159.3 (2)	N(36)–C(39)–C(40)	113.9 (5)
C(2)–Ru(1)–C(6)	135.2 (2)		

of the coordinated diethylamino ligand is with the H(36) atom pointing toward the CPD ligand, as indeed was borne out by the X-ray structure of 3 (Figure 1). Such a conformation, stabilized by the hydrogen bond, seems to exist also in solution (vide infra).

The phenyl groups are twisted with respect to the CPD ring plane (Figure 1). Consequently, the transmission of electronic effects from the phenyls to the metal atom must be attenuated. This is borne out by the fact that 2 and its *p*-chlorophenyl derivative exhibit very similar infrared spectra (CO region) as well as catalytic activity.

Selected X-ray structural parameters and spectral data for complexes 1–3 are compared in Tables III and IV. The CPD  $>C=O$  bond lengths indicate that the extent of polarization of this bond in the ground state follows the order

Table III. Crystallographic and Spectral Data for 1, 2, and 3

compd	>C=O angle, <sup>a</sup> deg	distance (Å)				
		>C=O	Ru—C6	Ru—C7,8,9,10 <sup>b</sup>	Ru—CO	C≡O
1 <sup>12</sup>	18.7	1.224	2.529	2.220	1.953, 1.926, 1.911	1.119, 1.132, 1.138
2 <sup>4</sup>	<1	1.287	2.371	2.235	1.885, 1.891	1.137, 1.140
3	6.1	1.247	2.417	2.220	1.879, 1.862	1.137, 1.133

<sup>a</sup> Torsional angle defined by the planes C7—C8—C9—C10 and C7—C6—C10—O6 (Figure 1). <sup>b</sup> Average bond distances.

Table IV. Spectral Data for 1, 2, and 3

compd	$\nu(\text{C}=\text{O})$ , cm <sup>-1</sup>	$\nu(\text{CO})$ , cm <sup>-1</sup>	$\delta(>\text{C}=\text{O})$ <sup>13</sup> C NMR
1 <sup>12</sup>	1655	2081, 2026, 2005	174.8
2 <sup>4</sup>	1550	2035, 2010, 1980, 1970	155.4
3	1565	2010, 1955	164.6

2 > 3 > 1. This is also evident from inspection of the infrared stretching frequency of the >C=O functionality of 3 which shifted 90 cm<sup>-1</sup> to lower wavenumbers relative to 1. Maximum planarity of the CPD ring is attained with highest polarization of the carbonyl in 2 (Table III). The <sup>13</sup>C NMR chemical shift values of the ring carbonyl also follow the above order, and the chemical shift of 3 is very close to the average value of 1 and 2.

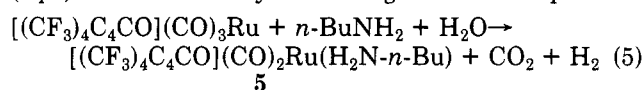
The substitution of a CO ligand in 1 by the nitrogen ligand that lacks  $\pi$ -acid properties places an excess electronic charge on the Ru atom of 3. This charge can be distributed among the remaining metal ligands by a back-donation mechanism (Ru → ligand) that should result in shortening of the relevant bonds. A moderate decrease in the Ru—CO bond lengths of 3 (average 1.870 (8) Å) relative to 1 (average 1.930 (15) Å) is noted (Table III). Concomitant elongation of the CO bond lengths in 3 is not observed, but the lowering of the CO infrared stretching frequencies of 3 relative to 1 (Table IV) does indicate weakening of these bonds. Identical distances (average) between Ru and the four butadiene C atoms of the CPD ring (C(7)—C(10)) of 1 and 3 are noted (Table III). This indicates no significant change in the back-donation from Ru → CPD upon substitution of CO by an amine ligand. The substantial decrease (>0.1 Å) in the Ru—C(6) distance of 3 relative to 1 is attributed to the hydrogen bond in the former complex which forces C(6) toward the metal atom and is also responsible for the observed flattening of the ring carbonyl and elongation of the >C=O bond distance (Table III).

The proton NMR spectrum of 3 indicates that the two methylene groups of the diethylamine ligand are chemically equivalent but that the two H atoms in each group are diastereotopic. Thus the CH<sub>2</sub> groups of 3 give rise to an AB pattern that is a part of an ABMX<sub>3</sub> system with spin coupling of H<sub>A</sub> and H<sub>B</sub> to the adjacent CH<sub>3</sub> (X<sub>3</sub>) group and unequal coupling with H—N (M). Due to partial overlap, only 11 lines are visible in a magnetic field of 360 MHz. Spin-decoupling experiments clearly confirmed the above assignments (see Experimental Section). Therefore the rigid tetrahedral geometry of the nitrogen atom of the diethylamine ligand in 3, as observed in the solid state (Figure 1), must also persist in solution. Nitrogen coordination to ruthenium and internal H bonding excludes inversion of the nitrogen atom as well as dissociation of the amine ligand on the NMR time scale; both processes would scramble the diastereotopic protons. It was found, however, that amine ligands do dissociate on moderate heating as amine—amine ligand exchange was observed.<sup>9</sup>

The molecular structure of 3 allows us now to assign analogous molecular structures to a series of dicarbonyl-(cyclopentadienone)ruthenium complexes with various secondary amines that exhibit infrared spectra very similar

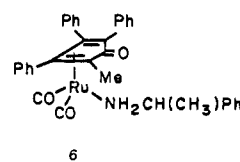
to that of 3.<sup>9</sup> Primary amine complexes,<sup>9</sup> viz., (Ph<sub>4</sub>C<sub>4</sub>CO)(CO)<sub>2</sub>Ru(NH<sub>2</sub>-*n*-Bu), must possess a similar molecular structure. The two H atoms (NH<sub>2</sub>) may either be symmetrically bound to the CPD oxygen atom or each singly bound but interchanging by slow rotation about the Ru—N bond. Thus, the NCH<sub>2</sub> NMR signal of the above complex exhibits a clean triplet after Rf saturation of the NH<sub>2</sub> signal, indicating no dissymmetry on the NMR time scale down to -20 °C.

Amine complexes of type 3 described here and also in our previous report<sup>9</sup> must owe their stability to the N—H...O hydrogen bond, discovered in the present work. Thus, complex 5 is readily formed at ambient temperature (eq 5) as determined by monitoring the infrared spectrum



of the toluene reaction solution (2045, 1985, 1590 cm<sup>-1</sup>). It could not, however, be obtained in the solid state as it rapidly decomposed upon attempted isolation using the usual procedure. We attribute this instability to the diminished strength of the N—H...O hydrogen bond in 5. The oxygen atom of the CPD carbonyl of 5 is less basic than that of 3 due to the four electron-withdrawing CF<sub>3</sub> groups situated on the CPD ring. This is reflected in an increase of 37 cm<sup>-1</sup> in the infrared stretching frequency of the CPD >C=O group of 5 relative to (Ph<sub>4</sub>C<sub>4</sub>CO)(CO)<sub>2</sub>Ru(H<sub>2</sub>NBu).<sup>9</sup>

A further understanding of the structure and stability of these complexes was sought by preparing and examining the chiral complexes 6. It was obtained as a solid by



reacting (*RS*)-1-phenylethylamine and [(*RS*)-(2-methyl-3,4,5-triphenylcyclopentadienone)]tricarbonylruthenium under the usual reaction conditions. The expected infrared stretching bands  $\nu(\text{CO})$  at 2010, 1950, and 1550 cm<sup>-1</sup> were recorded. The solid is a diastereomeric mixture as most of the <sup>1</sup>H NMR signals were doubled. This complex was prepared as a model for diastereomeric resolution by using, subsequently, optically active amines. However, neither crystallization nor column or thin-layer chromatography (Silica) could affect separation of the two racemic diastereomeric components; a single TLC spot of 6 was observed by using several solvent systems. Our inability to separate the mixture may be due either to accidental similarity of the physical properties of the two diastereomers or to diastereomeric equilibration on the isolation time scale. A plausible equilibration mechanism, viz., amine ligand dissociation, was ruled out as a solution of 6 in the presence of excess BuNH<sub>2</sub> was stable at room temperature for 48 h. and did not generate the analogous known butylamine complex.<sup>9</sup> This problem requires further study.

It is noteworthy that secondary amine complexes of type 3 are formed in the transalkylation reactions of tertiary

amines (eq 1). Furthermore they are extremely stable in the reaction solution; according to infrared measurements they are the only detectable complexes that persist during catalysis at 140 °C and can be isolated at the end of the reaction. Thus, dissociation of the CO ligand from **3** during catalysis (open vessel reaction) must be ruled out. In a recent report<sup>9</sup> we have proposed that the C–N bond cleavage occurs via an oxidative addition of NC–H to Ru and subsequent hydrolysis, although a carbene-type mechanism cannot be rigorously ruled out.

Finally, both **1** and **2** are also precatalysts in the oxidation of alcohols to aldehydes, ketones, and esters.<sup>1</sup> Structure **3** may now serve as a model for the primary interaction of alcohols with the present type of ruthenium complexes as described by **5**. Being a weaker  $\pi$  ligand than nitrogen, the oxygen atom in **5** is loosely bound to the metal, accounting for our failure to isolate stable alcohol complexes such as **7**. Nevertheless, in the light of the stability of **3**, the existence of analogous alcohol complexes as transient intermediates during catalysis is conceivable. The next step may involve the transfer of hydrogen and formation of Ru–O  $\sigma$  bond, **8**. Thus the CPD ligand actively participates in the oxidative-addition process.



## Experimental Section

**Dicarbonyl(diethylamine)(tetraphenylcyclopentadienone)ruthenium (3).** (Tetraphenylcyclopentadienone)tricarboxylruthenium (**1**) (0.29 g, 0.5 mmol), diethylamine (0.073 g, 1.0 mmol), water (2 mL), and toluene (15 mL) were stirred for 12 h at room temperature. The phases were separated, the organic solvent was removed in vacuo, and the residue was taken up with methylene chloride and chromatographed on silica. The fraction that emerged from the column with 5% EtOAc in  $CH_2Cl_2$  was crystallized from methylene chloride–hexane mixture to give crystals (green olive color) which were recrystallized from dichloromethane–hexane, dried, and subjected to X-ray diffraction analysis (Figure 1). The same complex was obtained when **1** (0.29 g, 0.5 mmol), triethylamine (0.101 g, 1.0 mmol), and water (2 mL) were heated in toluene (15 mL) under dinitrogen at 145 °C for 3 h, followed by evaporating of the amine and chromatographing the residue as described above. Anal. Calcd for  $C_{35}H_{31}NO_3Ru$ : C, 68.41; H, 5.05; N, 2.28. Found: C, 68.67; H, 5.16; N, 2.15. IR ( $CH_2Cl_2$ )  $\nu$  2010, 1955, 1565  $cm^{-1}$ ;  $^1H$  NMR ( $C_6D_6$ )  $\delta$  0.52 (t,  $J = 7.10$  Hz, 6 H,  $CH_3$ ), 1.53 (br quint,  $J = ca. 5$  Hz, 1 H, NH), 2.35 (m, 4 H,  $CH_2$ ), 6.76–7.03 (12 H, m, phenyls' protons), 7.27 (d,  $J = 7.10$  Hz, 4 H, phenyls' ortho protons), 8.12 (d,  $J = 7.24$  Hz, 4 H, phenyls' ortho protons). The signal at 1.53 ppm (NH) persists upon addition of  $D_2O$  and vanishes on addition of DCl. Rf saturation of the signal at 0.52 ppm ( $CH_3$ , M signal) resulted in the collapse of the multiplet (ABXM<sub>3</sub>) at 2.35 ppm ( $CH_2$ ) to an ABX pattern ( $J_{AB} = 12.6$  Hz,  $J_{AX} = 5.0$  Hz,  $J_{BX} = 5.8$  Hz). Rf saturation of the broad signal at 1.53 ppm (NH; X signal) resulted in the collapse of the above multiplet to a symmetrical 10-line spectrum (ABM<sub>3</sub>) with partial overlap of some of the lines ( $J_{AM} = J_{BM} = 7.10$  Hz).  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  13.8 ( $CH_3$ ), 51.5 ( $CH_2$ ), 83.2, 104.9 (C7–C10), 164.6 (C6), 202.0 (CO).

**(Butylamine)dicarbonyl[tetrakis(trifluoromethyl)cyclopentadienone]ruthenium (5).** This complex was prepared as described for **3** by using tricarbonyl[tetrakis(2,3,4,5-trifluoromethyl)cyclopentadienone]ruthenium (0.1 g, 0.186 mmol) and

butylamine (0.028 g, 0.372 mmol) in a toluene (6 mL) containing water (0.5 mL). The reaction was complete after 3 h at room temperature (TLC). The infrared spectrum of the dried toluene reaction solution, which gave a new and essentially single TLC spot, had bands at 2045, 1985, and 1595  $cm^{-1}$ . Attempted crystallization or chromatographic purification led to complete decomposition of the complex.

**Dicarbonyl(2-methyl-3,4,5-triphenylcyclopentadienone)(phenylethylamine)ruthenium (6).** A mixture of (2-methyl-3,4,5-triphenylcyclopentadienone)tricarboxylruthenium (0.224 g, 0.5 mmol) and 1-phenylethylamine (0.121 g, 1.0 mmol) in toluene (15 mL) and water (2 mL) was stirred overnight at room temperature. The organic phase was decanted and dried ( $MgSO_4$ ), the solvent evaporated, and the residue chromatographed (Silica). The column was eluted with mixtures of methylene chloride–petroleum ether (60–80); with methylene chloride there was obtained a fine crystalline powder (**6**), 0.18 g. Anal. Calcd for  $C_{34}H_{29}NO_3Ru$ : C, 67.98; H, 4.87; N, 2.33. Found: C, 67.71; H, 4.72; N, 2.18. IR ( $CH_2Cl_2$ ):  $\nu$  2010, 1950, 1550  $cm^{-1}$ ;  $^1H$  NMR ( $C_6D_6$ )  $\delta$  1.07 (d,  $J = 6.1$  Hz, 3 H, Me), 1.17 (d,  $J = 6.7$  Hz, 3 H, Me), 1.82 (s, 3 H, Me), 1.85 (s, 3 H, Me), 2.68 (m, br, 1 H, NH), 3.00 (m, br, 1 H, NH), 3.56 (m, 1 H, CH). The signals at 2.68 and 3.00 ppm slowly vanished (ca. 0.5 h) on addition of  $D_2O$  to the  $C_6D_6$  solution of **6**.

A solution of complex **6** (0.05 mmol) and dibutylamine (0.1 mmol) in toluene (2 mL) was kept at room temperature for 48 h. TLC monitoring has indicated no change in the composition of the reaction solution.

**X-ray Structure.** X-ray diffraction data were measured at ca. 18 °C on a CAD4 diffractometer equipped with a graphite monochromator, using Mo  $K\alpha$  ( $\lambda = 0.7107$  Å) radiation. The intensities of the reflections within  $0 < 2\theta < 50^\circ$  [ $(\sin \theta)/\lambda < 0.595$  Å<sup>-1</sup>] were collected by the  $\omega$ - $2\theta$  scan technique with a scan range of  $(1.0 + 0.3 \tan \theta)^\circ$ . All data were recorded at a constant 4 deg·min<sup>-1</sup> scan rate. Possible deterioration of the crystal was tested by detecting frequently the intensities of three standard reflections and was found negligible during the measurements. An empirical method was applied to correct the data for absorption.<sup>13</sup>

**Crystal Data for 3.**  $C_{35}H_{31}NO_3Ru$ ;  $M_r$ , 614.7; monoclinic;  $a = 10.386$  (2) Å,  $b = 19.953$  (3) Å,  $c = 14.664$  (7) Å;  $\beta = 103.07$  (4)°;  $V = 2960.1$  Å<sup>3</sup>;  $Z = 4$ ;  $D_{calcd} = 1.379$  g·cm<sup>-3</sup>;  $F(000) = 1264$ ;  $\mu(Mo K\alpha) = 5.52$  cm<sup>-1</sup>; space group  $P2_1/c$ .

The structure was solved by a combination of direct methods and Fourier techniques (MULTAN80). The refinement was carried out by large-block least squares (SHELX76), including the atomic coordinates and anisotropic thermal parameters of all the non-hydrogen atoms. Most hydrogens were introduced into the structure factor computations in calculated positions, the methyls being treated as rigid groups in the final refinement. The H atom attached to nitrogen was unambiguously located in the difference Fourier map. The final discrepancy indices at the end of the refinement were  $R = 0.042$ ,  $R_w = 0.042$ , and goodness of fit = 1.31 e for 3604 unique observations above the intensity threshold of  $3\sigma_I$ . The final difference Fourier maps showed no indications of incorrectly placed or missing atoms. The refined atomic parameters are listed in Table I. Bond lengths and bond angles within the molecule are unexceptional.

**Registry No.** **1**, 12321-08-3; **3**, 115512-11-3; **5**, 115512-12-4; **6**, 115512-13-5;  $Et_2NH$ , 109-89-7;  $Et_3N$ , 121-44-8;  $[(CF_3)_4C_4CO](CO)_3Ru$ , 54362-20-8;  $n$ -BuNH<sub>2</sub>, 109-73-9; (*RS*)-PhCH( $CH_3$ )-NH<sub>2</sub>, 618-36-0; (2-methyl-3,4,5-triphenylcyclopentadienone)tricarboxylruthenium, 115512-14-6.

**Supplementary Material Available:** Tables of atomic coordinates of the hydrogen atoms and anisotropic thermal parameters (2 pages); a listing of structure factors (13 pages). Ordering information is given on any current masthead page.

(13) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.