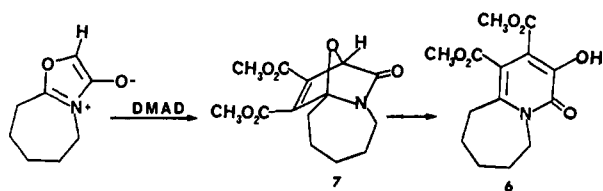**Scheme II**

Figure 2 shows the UV spectrum of neat 1-(2-chloroacetyl)-caprolactam taken shortly after preparation and during reaction at ambient temperature. The appearance of bands at 270 and 320 nm is similar to that reported by Griot and Frey, who studied the UV behavior of 7-hydroxy-8-oxa-1-azabicyclo[5.3.0]decanone (5) in sulfuric acid solution.[7] They interpreted the appearance of these bands as indication of the formation of the 5-hydro-1,3-oxazolium 4-oxide intermediate 2 as shown in Scheme I. This compound could also result from cyclization of the 2-chloroacetyl side chain of the 1-(2-chloroacetyl)lactam in an O-alkylation process as shown. We propose that further reaction of 2 with chloride anion and liberation of HCl results in the formation of the mesoionic 1,3-oxazolium 4-oxide or "isomunchnone" 3. Compounds of this type have been reported[8,9] to be unstable and highly reactive in 1,3-dipolar addition reactions with acetylenic and carbonyl compounds and alcohols.[10–12] This isomunchnone was trapped by reacting 1-(2-chloroacetyl)caprolactam with dimethylacetylenedicarboxylic (DMAD).[13] The crystalline product isolated from this reaction proved to be 7,8,9,10,11-pentahydro-3-hydroxy-4,5-bis(methoxycarbonyl)cyclohepta[a]pyridin-2-one (6). This compound results from rearrangement of the 1,3-dipolar cycloaddition product 7 as shown in Scheme II. The proposed polymerization process shown in Scheme I involves O attack of the isomunchnone 3 on the hydro-1,3-oxazolium 4-oxide 2 followed by successive propagation steps involving Michael-type addition of the isomunchnone 2 to the unsaturated moiety 4. To our knowledge, this represents the first reported polymerization involving a mesoionic 1,3-oxazolium intermediate.

The caprolactam-based polymer is white to yellow in color and has inherent viscosities of 0.07 to 0.03 dL/g (0.5 g/dL in dimethyl sulfoxide) depending upon the polymerization temperature. The 2-piperidone-based polymer is deep red in color, and the 2-aza-cyclooctanone-based polymer is yellow-gold.[14] Viscosities of these polymers are comparable to those of the caprolactam polymers. All polymers are soluble in a wide variety of organic solvents including methanol, benzene, and tetrahydrofuran. They are insoluble in water, appear to be noncrystalline, and do not possess

sufficient molecular weight to form films or fibers. Further work is needed to confirm the proposed polymerization mechanism and improve product molecular weights.

Structure and Reactivity of [Ti{Ru(CO)₂(C₅H₅)}(NMe₂)₃]: A Direct Early–Late-Transition-Metal Bond Formed by Amine Elimination

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Condensation reactions in which a small molecule is eliminated have been recommended as a facile method for the preparation of heteronuclear metal–metal bonds.[1] We are exploring amine elimination (eq 1) as a potential method for forming bonds between

early and late transition metals. Lappert and co-workers reported

$$M-NR_2 + M'-H \rightarrow M-M' + R_2N-H \qquad (1)$$

that Mo–Ti bonds were formed by reactions of [MoH(CO)₃(Cp)] with [Ti(NMe₂)(OCHMe₂)₃] or [Ti(NMe₂)(Cp)₂]₂.[2] However, in our hands [MoH(CO)₃(Cp)] invariably leads to "isocarbonyl" (Σ-CO)[3] linkages of the type Mo–CO–M$_{early}$, as illustrated by the structure of [Zr{(μ-CO)Mo(CO)₂(Cp)}₂(NEt₂)₂(NHEt₂)]₂,[4a] and many related compounds.[4b] We report here the first unambiguous example of a direct bond between an early and a late transition metal formed by amine elimination.

A solution of 2.35 mmol of [RuH(CO)₂(Cp)] (prepared from 0.50 g of [Ru₃(CO)₁₂] and excess cyclopentadiene)[5] in ca. 150 mL of n-heptane was gradually added to 0.50 g (2.23 mmol) of [Ti(NMe₂)₄].[6] The resulting yellow solution was stirred for 6 h at room temperature, filtered to remove a slight cloudiness, and then reduced to an oil and dried in vacuo for ca. 12 h. A minimum of toluene was added to dissolve the product, which crystallized upon concentration. Washing with a small amount of cold heptane and drying in vacuo gave 0.40 g (45%) of yellow [Ti{Ru(CO)₂-(Cp)}(NMe₂)₃] (I).[7]

Spectroscopic characterization, particularly the absence of an infrared absorption at ca. 1600 cm⁻¹,[3] suggested formation of a direct Ru–Ti bond. This was confirmed by an X-ray diffraction study.[8] A plot of the structure of I is presented in Figure 1, and

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(9) Potts, K. T.; Marshall, J. *J. Chem. Soc., Chem. Commun.* **1972**, 1000.

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(13) Freshly prepared 1-(chloroacetyl)caprolactam, 6.00 g (0.0317 mol), was combined with 6.75 g (0.0475 mol) of DMAD and heated for 2 h at 80 °C under moderate vacuum. The ether-insoluble fraction was recrystallized from methanol to yield 1.56 g of 6 (16.7%): mp 200–201 °C; IR 3213, 1729, 1644, 1609, 1440, 1251, 1230 cm⁻¹; UV 315 nm (ε 9.2 × 10³), 277 (9.1 × 10³), 220 (1.5 × 10⁴); ¹H NMR δ 9.85 (1 H, s; exchanged D₂O), 4.37 (2 H, m), 3.74, 3.68 (6 H, s) 2.94 (2 H, m), 1.65 (6 H, m); ¹³C NMR (off-resonance decoupling) δ 166.3 (s), 165.4 (s), 157.9 (s), 143.6 (s), 142.0 (s), 117.7 (s), 107.2 (s), 52.4 (q), 43.8 (t), 28.8 (t), 28.2 (t), 27.0 (t), 26.2 (t). Long-range C–H coupling and COSY were used to assign the structure unambiguously. Anal. Calcd for C₁₄H₁₇NO₆: C, 56.95; H, 5.76; N, 4.75. Found: C, 56.82; H, 5.90; N, 4.82.

(14) The color experienced in some of the polymers is reflected in broad UV absorbances centered at 280 and 340 nm which are found in samples of caprolactam and azacyclooctanone polymers prepared at high temperature only. They are presumably due to side reactions of the polymer as it is formed. For the 2-piperidone-based polymer, the red color is seen in samples prepared at ambient and elevated temperature and cannot be removed by extraction. The 1-(2-chloroacetyl)piperidone monomer showed strong absorbances at 280 and 375 nm even after 2-months storage at ambient temperature. This may be indicative of a highly stabilized isomunchnone chain end or intermediate for this particular monomer.

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(5) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

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(7) Spectroscopic and physical data for I: mp 82–84 °C; IR (heptane) 1972 (s), 1911 (s) cm⁻¹; ¹H NMR (C₆D₆, 90 MHz) δ 4.81 (s, 5 H, Cp), 3.12 (s, 18 H, NMe₂); mass spectrum, m/e 403 (M⁺), 375 (–CO), 347 (–2CO), 360 (–CO, –CH₃), 332 (–2CO, –CH₃), 224 ([Ru(CO)₂(Cp)]).

Communications to the Editor

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Table I. Selected Bond Lengths and Angles for [Ti{Ru(CO)$_2$(Cp)}(NMe$_2$)$_3$]

bond	length, Å	atoms	angle, deg	atoms	angle, deg
Ru–Ti	2.663 (1)	Ti–Ru–C1	80.2 (2)	N2–Ti–N3	109.6 (2)
Ru–C1	1.859 (8)	Ti–Ru–C2	83.0 (2)	Ru–C1–O1	178.1 (6)
Ru–C2	1.840 (7)	Ti–Ru–CpO^a	119.1 (2)	Ru–C2–CO	175.4 (7)
Ti–N1	1.878 (6)	C1–Ru–C2	89.7 (3)	Ti–N1–C3	118.6 (5)
Ti–N2	1.888 (5)	Ru–Ti–N1	109.9 (2)	Ti–N1–C4	130.0 (5)
Ti–N3	1.888 (5)	Ru–Ti–N2	109.6 (2)	Ti–N2–C5	115.9 (4)
C1–O1	1.149 (9)	Ru–Ti–N3	113.1 (2)	Ti–N2–C6	131.5 (5)
C2–O2	1.159 (9)	N1–Ti–N2	107.0 (2)	Ti–N3–C7	116.6 (5)
Ru–CpO^a	1.945 (7)	N1–Ti–N3	107.6 (3)	Ti–N3–C8	131.3 (5)

^{a} CpO is the centroid of the cyclopentadienyl ring.
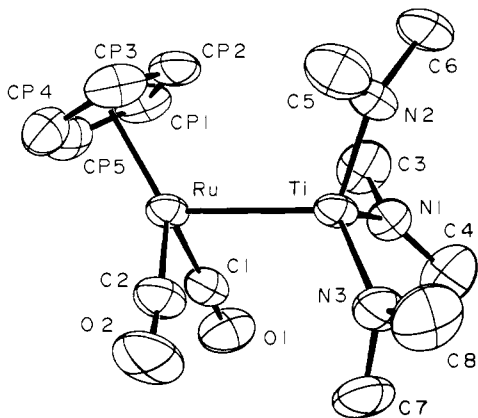

Figure 1. ORTEP[18] plot of [Ti[Ru(CO)$_2$(Cp)](NMe$_2$)$_3$] with 50% probability ellipsoids.

selected distance and angles are found in Table I. The most striking feature is the direct Ru–Ti bond. The only other direct Ti to late-transition-metal bond is present in [Ti{Co(CO)$_4$}{OCCo$_3$(CO)$_9$}(Cp)$_2$], with a Ti–Co distance of 2.614 Å.[9–11] Coordination about the titanium atom (a formal 8-electron center) in I is tetrahedral, with no intermolecular association. The Ti–N bonds are rather short, and the Ti–NMe$_2$ groups are planar, suggesting effective nitrogen to titanium π-donation. The C2–Ru–Ti–N3, Cp(centroid)–Ru–Ti–N2, and C1–Ru–Ti–N1 torsion angles are respectively 10.0°, 21.7°, and 39.3°; this near eclipsing of carbonyl C2–O2 and the N3 amide group may explain why Ru–Ti–N3 is more obtuse than the corresponding N1 and N2 angles. For methyl carbons that are "syn" to ruthenium (C3, C5, and C7 with d(Ru–C) averaging 4.10 Å) the Ti–N–C angles are about 14° more acute than for methyl carbons that are "anti" to ruthenium (C4, C6, C8 with d(Ru–C) averaging 4.91 Å). As the molecule is not particularly crowded, we do not believe that this is a steric effect. The [Ru(CO)$_2$(Cp)] moiety is structurally

very similar to [Zr{Ru(CO)$_2$(Cp)}(OCMe$_3$)(Cp)$_2$],[10a] [Zr{Ru(CO)$_2$(Cp)}$_2$(Cp)$_2$],[10b] and [Ru(CONH$_2$)(CO)$_2$(Cp)].[12] There is no interaction between the electron-deficient titanium atom and the carbonyl ligands (the nonbonding distances from Ti to C1, O1, C2, and O2 are respectively 2.975, 3.684, 3.046, and 3.818 Å; Shriver's Ω parameter[3] for carbonyls C1–O1 and C2–O2 is respectively 2.24 and 2.22).

Similar compounds are formed by reacting [RuH(CO)$_2$(Cp)] with [Ti(NMe$_2$)$_n$(OCHMe$_2$)$_{4-n}$] (n = 1–3) in a 1:1 mole ratio.[13] These Ru–Ti compounds are yellow liquids which give molecular ions in their mass spectra. Remarkably, [Ti{Ru(CO)$_2$(Cp)}(OCHMe$_2$)$_3$] can even be vacuum distilled (with significant loss) at 135 °C (0.02 torr). Despite their thermal stability, these compounds are extremely oxygen and water sensitive, decomposing upon contact with air. Their infrared spectra show a gradual increase in CO stretching frequencies and their proton NMR spectra show a shift of the cyclopentadienyl resonance to lower field as amide ligands are replaced by alkoxide ligands, reflecting the greater π-donor ability of amides. The CO stretching frequencies of the ruthenium–titanium compounds fall between those of K[Ru(CO)$_2$(Cp)] (1905, 1760, 1685, 1580 cm^{-1})[10] and [Ru(GeMe$_3$)(CO)$_2$(Cp)] (2016, 1957 cm^{-1})[14] and are slightly higher than those of Casey's ruthenium–zirconium compounds (ca. 1950, 1880 cm^{-1}),[10] suggesting that the Ru–Ti bonds are less highly polarized than in Casey's compounds.

We have begun to investigate the reactivity of the Ru–Ti compounds. [Ti{Ru(CO)$_2$(Cp)}(NMe$_2$)$_3$] reacts rapidly with excess Me$_3$COH (C$_6$D$_6$, room temperature) to give [RuH(CO)$_2$(Cp)] quantitatively, followed by a slower reaction leading to [Ti(OCMe$_3$)$_4$] and NHMe$_2$. [MoH(CO)$_3$(Cp)] similarly cleaves the Ru–Ti bond, leading immediately to [RuH(CO)$_2$(Cp)] and a Mo–Ti compound with δ(Cp) 5.35.[4a]

We believe that the formation of *direct* Ru–Ti bonds, rather than "isocarbonyl" linkages as observed for molybdenum, is largely a consequence of the greater basicity of [Ru(CO)$_2$(Cp)]$^-$ relative to [Mo(CO)$_3$(Cp)]$^-$.[15] Although the hypothetical directly bonded molybdenum compounds would be pseudo-seven-coordinate, they would not be unreasonably crowded, as evidenced by structurally characterized, Mo–Zn bonded [Mo{ZnBr(THF)$_2$}(CO)$_3$(Cp)].[16] Phosphine-substituted metal hydrides such as [RuH(PPh$_3$)$_2$(Cp)] and [FeH(dppe)(Cp)] might thus be even more likely to form stable, direct early–late metal bonds, but they do not react with zirconium amides even under forcing conditions,[17] probably be-

(8) Crystal data for I: a single crystal was mounted in a 0.5-mm glass capillary in a Vacuum Atmospheres drybox, sealed temporarily with silicone grease, removed, and immediately flame sealed. Data were collected on an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation; space group $P2_1/c$, Z = 4, a = 13.898 (3) Å, b = 8.576 (3) Å, c = 15.814 (3) Å, β = 111.24 (2)°, V = 1756.8 Å^3, ρ_{calcd} = 1.52 g cm^{-3}, ν = 13.14 cm^{-1}. 3583 reflections were collected, and of these 3016 with $(F_0)^2 \geq 3\sigma(F_0)^2$ were used. The ruthenium atom was located by Patterson methods, and the remaining atoms by difference Fourier methods, including several hydrogen atoms. Remaining hydrogen atoms were placed in calculated positions with d(C–H) = 1.0 Å. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were held fixed with B = 6.0 Å^3. Full-matrix least-squares refinement led to R = 6.3% and R_w = 7.6%.

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(10) Direct Ru–Zr bonds (2.910–2.948 Å) have been found in [Zr{Ru(CO)$_2$(Cp)}(OCMe$_3$)(Cp)$_2$] and [Zr{Ru(CO)$_2$(Cp)}$_2$(Cp)$_2$], which were prepared from K[Ru(CO)$_2$(Cp)] and the corresponding zirconium chlorides: (a) Casey, C. P.; Jordan, R. F.; Rheingold, A. P. *J. Am. Chem. Soc.* **1983**, *105*, 665. (b) Casey, C. P.; Jordan, R. F.; Rheingold, A. P. *Organometallics* **1984**, *3*, 504.

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(13) Spectroscopic and physical data. [Ti{Ru(CO)$_2$(Cp)}(OCHMe$_2$)$_3$], bp 135 °C (0.02 torr). Anal. Calcd for C$_{16}$H$_{26}$O$_5$RuTi: C, 42.95; H, 5.87. Found: C, 41.86; H, 6.19. ^{1}H NMR (C$_6$D$_6$, 90 MHz) δ 5.02 (s, 5 H, Cp), 4.63 (sept, 3 H, C*H*Me$_2$, J = 6.0 Hz), 1.29 (d, 18 H, Me); IR (heptane) 1983 (s), 1928 (s) cm^{-1}; mass spectrum, m/e 449 (M$^+$), 392 (–2CO), 225 ([Ti(OCHMe$_2$)$_3$]), 224 ([Ru(CO)$_2$(Cp)]). [Ti{Ru(CO)$_2$(Cp)}(NMe$_2$)(OCHMe$_2$)$_2$]. ^{1}H NMR (C$_6$D$_6$, 90 MHz) δ 4.95 (s, 5 H, Cp), 4.64 (sept, 2 H, J = 6.0 Hz), 3.33 (s, 6 H, NMe$_2$), 1.29 (d, 12 H, Me); IR (heptane) 1975 (s), 1921 (s) cm^{-1}; [Ti{Ru(CO)$_2$(Cp)}(NMe$_2$)$_2$(OCHMe$_2$)] ^{1}H NMR (C$_6$D$_6$, 90 MHz) δ 4.94 (sept, 1 H, CHMe), 4.88 (s, 5 H, Cp), 3.32 (s, 12 H, NMe$_2$), 1.49 (d, 6 H, Me); IR (heptane) 1973 (s), 1917 (s) cm^{-1}.

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cause of their extremely low acidity.

In summary, we have shown that amine elimination is an effective way to form direct early–late-transition-metal bonds under mild conditions. Formation of compounds with several early–late metal bonds and the reactivity of the early–late metal complexes are now under investigation.

Supplementary Material Available: Listings of experimental and calculated structure factors (Table II) and positional and thermal parameters (Table III–V) (20 pages). Ordering information is given on any current masthead page.

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(19) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

Effects of Molecular Organization on Photophysical Behavior. Excimer Kinetics and Diffusion of 1-Pyrenedecanoic Acid in Lipid Monolayers at the Nitrogen–Water Interface[1]

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Here we report the time resolved behavior of pyrenedecanoic acid excimers in spread phospholipid monolayers at the air–water interface. It is well established that pyrene excimer formation is a diffusion-controlled process[2] and prominent use has been made of excimer fluorescence to measure the diffusion of this probe through various host media, especially those related to biological membranes.[3] In the present study, interactions of the pyrene-bearing probe, 1-pyrenedecanoic acid (PDecA), have been compared as functions of probe concentration and hydrocarbon structure of the host lipid to the character of the lipid environment.

A rectangular Teflon Langmuir trough, maintained at 22 °C and 90+% relative humidity, was used. Time-resolved measurements were made with a modified PRA (Photochemical Research Associates) single photon lifetime apparatus using a PRA nitromite laser as the excitation source.[4] Excimer behavior was monitored at 480 nm.

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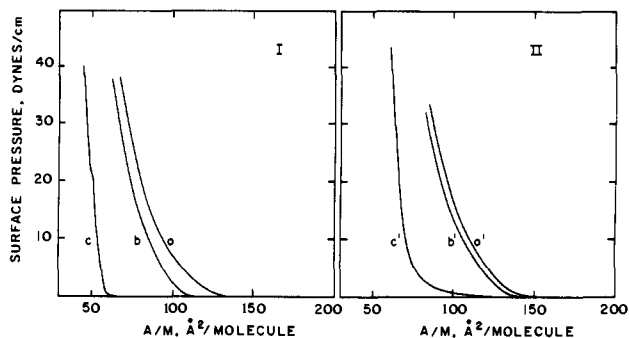

Figure 1. Force–area isotherms for DLP (a), DOP (b), and DSP (c) without (I) and then with (II) equimolar PDecA. Horizontal axis, area per lipid molecule.
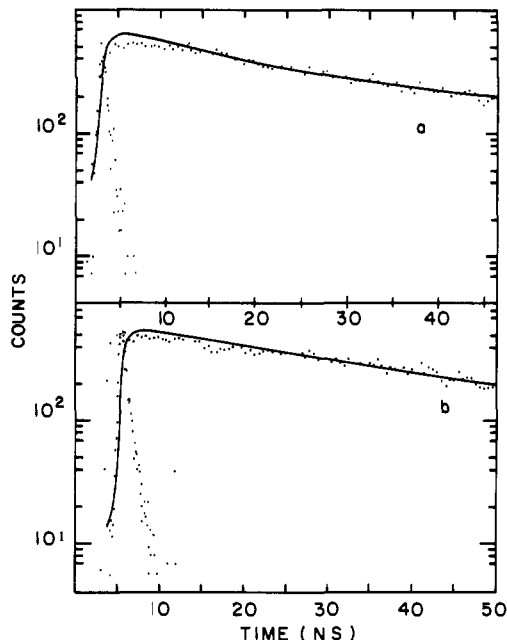

Figure 2. Lifetime measurements at the N₂–water interface for spread monolayers of PDecA in DOP at ratios of (a) 1:1.5 (τ = 18 ns) and (b) 1:3 (τ = 33 ns). Excitation was with a 300-ps N₂-laser puluse (λ = 337 nm) and emission was monitored at 480 nm. The curve fits provided are based on convolution with a single exponential. Attempts to obtain two exponential fits were unsatisfactory. Measurements were taken at surface pressures of 5 dyn/cm.

Figure 1 illustrates the force–area isotherms—with and without equimolar probe—for monolayers of the three lipid systems examined: dilinoleoyl-L-phosphatidylcholine (DLP), dioleoyl-L-phosphatidylchloline (DOP), and distearoyl-L-phosphatidylcholine (DSP). The pure lipid data agree well with those reported in the literature.[5] The probe itself, at these levels, may be seen to force an increase of about 10–15% in lipid–lipid intermolecular separation under the surface pressures at which lifetime measurements were conducted (5 dyn/cm).

Time-resolved fluorescence measurements of mixed PDecA–lipid monlayers exhibit two features at 480 nm: a very fast rise in excimer intensity and a dependence of the excimer decay on PDecA mole fraction in the layer. Figure 2 illustrates these features (see caption for details). Plots of apparent decay rate vs. mole fraction are given in Figure 3. The lifetime will be subject to an error of ±5%.

An interpretation of this behavior may be made by employing the approach of Birks and co-workers, developed to explain photophysical behavior of pyrene in concentrated hexane solutions.[6]

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