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Rhodium A-Frame Promoted Decomposition of Alkylnitrosoureas and Isocyanate Formation

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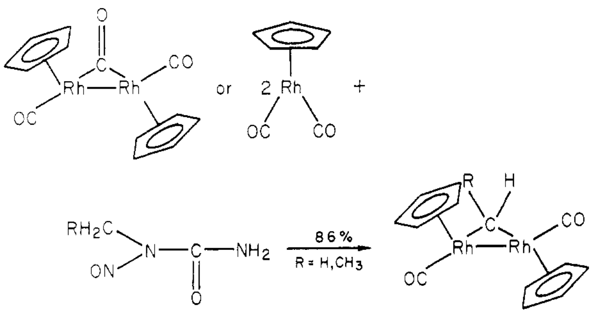
Summary: The Rh(0) A-frame complex $Rh_2(\mu\text{-}CO)(CO)_2(dpm)_2$ promotes the decomposition of alkylnitrosoureas leading to the formation of $Rh_2(NCO)_2(CO)_2(dpm)_2$ in >95% isolated yield and gaseous products including H_2, CO, and carbene derived products. The complex $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$ reacts similarly forming the μ-NCO complex $[Rh_2(\mu\text{-}NCO)(CO)_2(dpm)_2]^+$.

In the presence of transition-metal complexes, alkylnitrosoureas (ANU, $RN(NO)CONH_2$; MNU, R = Me; ENU, R = Et) have been shown to act as mild nitrosylating agents and carbene sources, presumably through the intermediacy of diazoalkanes. These two different reaction pathways have been reported by Herrmann and coworkers,[1] for closely related cyclopentadienyl carbonyl complexes of rhodium and cobalt as shown in eq 1 and 2. In this paper we report that certain binuclear complexes promote the decomposition of ANU leading to the formation of isocyanate complexes and reduction products including H_2 and, when R = Me, methane.



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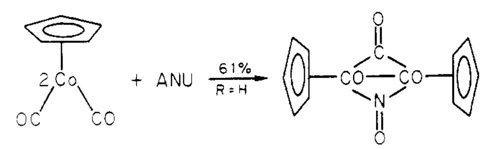

(2)

In a typical experiment, the tricarbonyl A-frame complex $Rh_2(\mu\text{-}CO)(CO)_2(dpm)_2$, **1**,[3] reacts with MNU or ENU in dried, degassed benzene at 70 °C to form the diisocyanate complex $Rh_2(NCO)_2(CO)_2(dpm)_2$, **2**,[4] which precipitates from solution in >95% isolated yield, along with CO, CO_2, H_2, and carbene-derived arbene-derived products which are discussed further below. When the bridging hydride complex $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$, **3**,[3] is employed, the reaction with MNU yields the bridging isocyanate species $[Rh_2(\mu\text{-}NCO)(CO)_2(dpm)_2]^+$, **4**, as the metal complex product (>95% isolated yield obtained by precipitation from the reaction solution). In these reactions, the binuclear complexes promote ANU decomposition. In their absence, MNU and ENU show no evidence of decomposition during the time period in which the reaction with metal complex occurs. Complex **2** had been synthesized previously by a metathesis procedure,[5] while complex **4** can be prepared from **2** independently by reaction with 1 equiv of $AgBF_4$[6] or *p*-toluenesulfonic acid.

The gaseous products from the reaction of **1** and MNU are shown as a function of time in Figure 1.[7] Only H_2 and CH_4 correspond to reduction products in this reaction in which the metal centers are oxidized from Rh(0) to Rh(I).[8] The origins of both H_2 and CH_4 have been probed by using selectively labeled MNU. When $MeN(NO)COND_2$ (65% labeled) is employed in the reaction with **1**, D_2, HD, and H_2 are obtained, as is a mixture of CH_2D_2, CH_3D, and CH_4. Clearly, the N-bound protons of the MNU substrate serve as a common origin for H_2 and half of the hydrogen atoms in the methane produced. The remaining part of the methane molecule is thought to arise from methylene carbene. This conclusion is supported by the observation of C_2H_4 in the product gases and by the results of other ANU decomposition experiments.

The observation of CO in the product gases during early stages of the reaction suggests that CO loss from **1** occurs concomitant with or prior to the promotion of MNU decomposition. This is supported by complete inhibition of the reaction of **1** + MNU when carried out under CO (1 atm). The subsequent conversion of CO to CO_2 which is seen in Figure 1 appears to be a secondary process unrelated to ANU decomposition and the carbene forming steps of the reaction.

When ENU is reacted with **1**, the product gases include butenes, ethylene, CO, CO_2, and H_2 as the only reduction product, and when a mixture of MNU and ENU is employed, propylene is found to be a major component of the hydrocarbon products. This evidence thus supports the formation of carbenes, or at least their diazoalkane precursors, in the decompositions of ANU promoted by **1**. (A reviewer has suggested that olefins may form via the reaction of diazoalkane with the conjugate acid alkyldiazonium cation which can form in this system.) However, only with MNU is a reduced hydrocarbon, CH_4, formed as a primary product; with ENU, only H_2 is obtained.

The reaction of **3** with MNU produces a mixture of gaseous products which is virtually identical with that shown in Figure 1 during the first 6 h. Subsequently, ethane is produced with a corresponding decrease in C_2H_4 and H_2. Since **3** is formed from **1** by reversible protonation,[3] the reaction may proceed via the same pathway as that followed by **1** during the first several hours. The ethane produced is a secondary product and arises because of the ability of **4** to function as a hydrogenation catalyst. This was verified separately by heating a benzene solution of **4** under C_2H_4 and H_2 (1:1, 700 torr, 60 °C). C_2H_6 was observed to form at an initial rate of 0.6 turnovers/h.

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[1] (a) Herrmann, W. A.; Kruger, C.; Goddard, R.; Bernal, I. *J. Organomet. Chem.* **1977**, *140*, 73. (b) Herrmann, W. A.; Bernal, I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 172.

[2] Typical reactions amounts: 0.21 g (0.2 mmol) of $Rh_2(\mu\text{-}CO)(CO)_2(dpm)_2$, **1**, 0.21 g (2 mmol) of MNU, or 0.23 g (2 mmol) of ENU and 40 mL of benzene in a 140-mL reaction flask.

[3] Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637. Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.*, in press.

[4] IR (Nujol): ν_{CO} 1975 (vs) cm^{-1}; ν_{NCO} 2235 (vs) cm^{-1}. Anal. Calcd for $Rh_2P_4N_2O_4C_{54}H_{44}$: C, 58.2; H, 4.0; N, 2.5; P, 11.1. Found: C, 57.8; H, 4.1; N, 2.6; P, 11.3.

[5] Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1981**, 228.

[6] IR (Nujol): ν_{CO} 1994 (s), 1979 (vs) cm^{-1}; ν_{NCO} 2205 (vs) cm^{-1}; ν_{BF} 1057 (s) cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$) δ 7.90 (m, 8), 7.51 (m, 16), 7.36 (m, 8), 4.24 (m, 2), 4.18 (m, 2).

[7] Gases were analyzed on a Hewlett-Packard 5700A Gas Chromatograph with thermal conductivity detectors and helium carrier gas (40 mL/min). Gas samples (0.5 mL) were withdrawn from the reaction flask through septa using a gas-tight Pressure-Lok syringe. The following columns were used: H_2, CO, 2 ft × $^1/_4$ in. 5A molecular sieves and 12 ft × $^1/_4$ in. Porapak Q; CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, 12 ft × $^1/_4$ in. Porapak Q; C_4H_8, 12 ft × $^1/_4$ in. 30% Dimethylsulfolane on Chromosorb P. H_2, CH_4, CO_2, and C_2H_4 were also identified by mass spectrometry on a Du Pont 490B mass spectrometer.

[8] Approximately 65% of the reduction products based on the oxidized metal product have been accounted for. Solubility of the gases in the solvent was not taken into account, and the liquid phase of the reaction was not fully analyzed for other reduction products.

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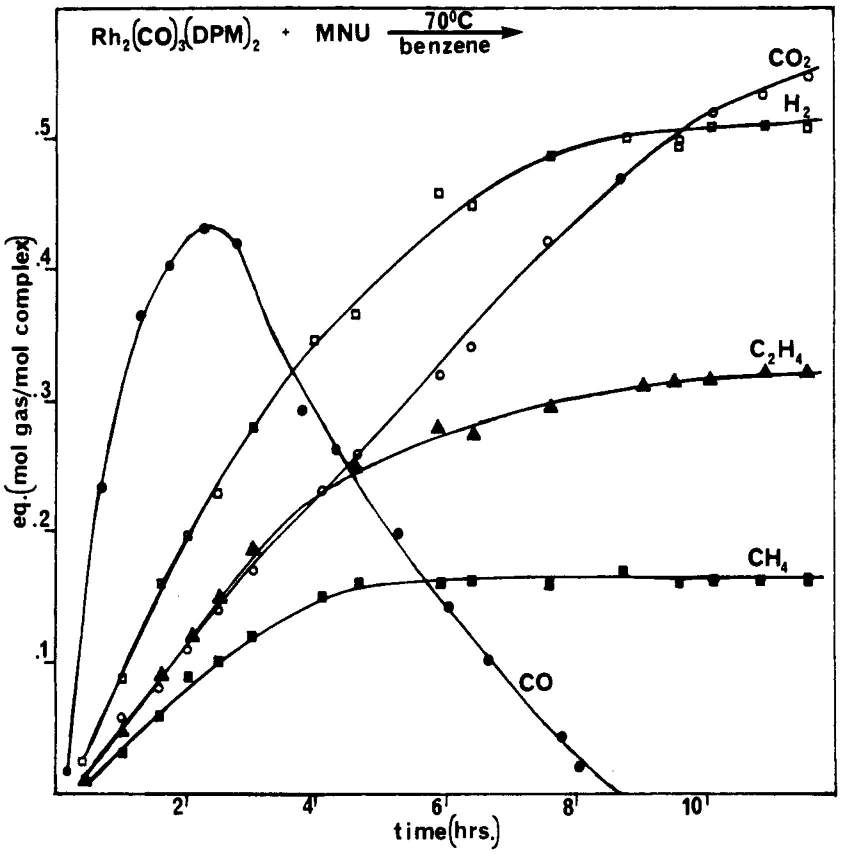
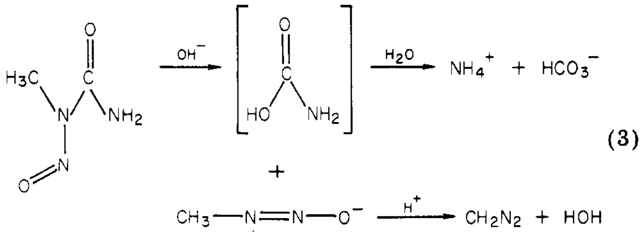


Figure 1. Evolution of gases produced vs. time for the reaction of 1 + MNU.

Sanger has recently shown that the chloro analogue of 4 catalyzes alkene and alkyne hydrogenations,[9] and it is probable that the two systems function in a similar manner.

The stoichiometry of the reaction of 1 with MNU was also examined by using MNU:1 ratios of 1, 2, 5, 10, and 100. In the first instance the metal complex products were a mixture of 1 and 2 only. With ratios of 2 and greater the sole complex product was 2, and with ratios greater than 2 significantly greater amounts of gaseous products were *not* observed during the first 6 h of the reaction, indicating that while MNU decomposition was being promoted, actual catalysis was not occurring. It is evident that the promotion of ANU decomposition by 1 occurs prior to carbene formation and is intimately tied to the generation of the isocyanate ligand in the product complexes. In the aqueous base-promoted decomposition of ANU,[10] hydroxide attack on the urea carbon leads to the formation of unstable carbamic acid and alkyl diazotate which then proceeds to diazoalkane via protonation and dehydration as shown in eq 3. A role similar to OH^- can be envisioned for 1 in the present study in which the resultant complex A loses H^+ (to form B) followed by a proton shift to form a rhodium(II) hydrido isocyanate intermediate, C. These proposed steps are summarized in eq.4. This proposal for isocyanate formation in which A–C are not observed directly receives support from the reaction of 1 with an amide-containing substrate having initial reactivity similar to ANU and from literature precedented transformations of amides. Thus, complex 1 reacts with phenylcarbamate, $PhOCONH_2$, to produce the diisocyanate complex 2 in 80% yield along with equivalent amounts of CO and H_2. The conversion of the metallocarboxamide A to the intermediate C is akin to a partial Hofmann degradation of an amide to R–NCO and has more direct precedence in Lindenberg's study[11] of the reaction of metal carbonyl complexes with hydroxylamine



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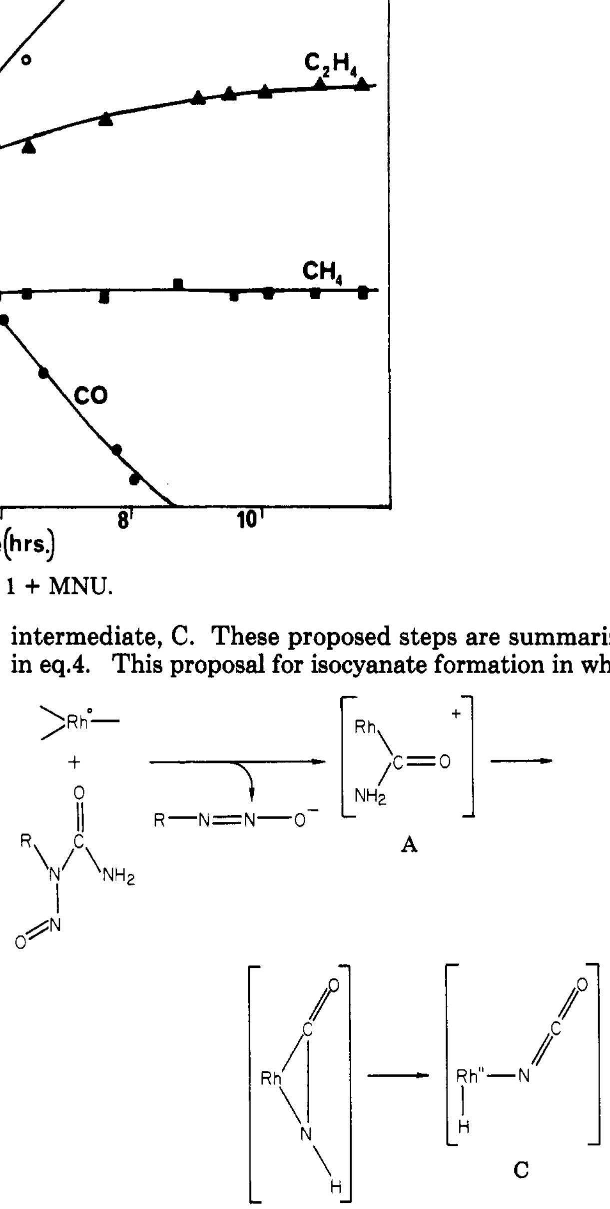

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[10] Snyder, J. K.; Stock, L. M. *J. Org. Chem.* **1980**, *45*, 1990.

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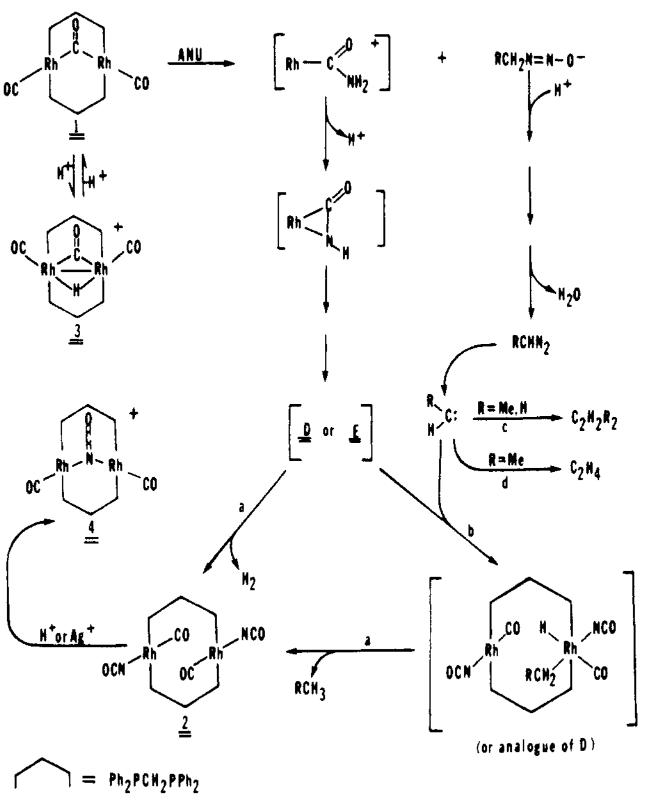
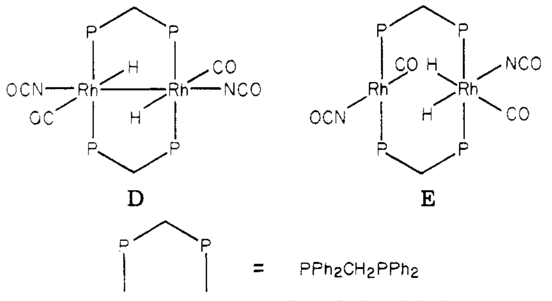
Scheme I



a,reductive elimination; b,carbene insertion; c,dimerization; d,internal rearrangement

followed by rearrangement. An alternative to eq 4 in which diazoic acid, R—N=N—OH, serves as the leaving group and formulations of A and B differ slightly from the formulations above cannot be ruled out at this time. However, the possibility of a direct reaction of complex 1 with preformed alkyl isocyanate, which is known to form in ANU decompositions,[12] was ruled out by a control experiment in which a benzene solution of 1 and MeNCO is heated at reflux and yields quantitative recovery of 1.

The production of H_2 follows a reductive elimination path. Since both 1 and 2 are binuclear and since 2 e⁻ are needed for H_2 formation, we propose that the species penultimate to H_2 generation has either structure D or E.



The former has metal–metal bonded Rh(II) centers and is analogous to binuclear oxidative addition products observed by Balch[13] while the latter has a Rh(I) Rh(III) structure similar to an iridium system reported by Pignolet and Wang.[14] The formation of methane is readily envisioned from D or E by CH_2 insertion into one of the Rh–H bonds followed by reductive elimination. Half of the hydrogens of the CH_4 product thus originate as the N-bound protons of the MNU substrate consistent with our labeling experiment.

The reaction chemistry thus shows that the binuclear complex 1 promotes ANU decomposition leading to the diisocyanate complex 2 and carbene formation. The hydride intermediate formed following promotion of ANU decomposition may then reductively eliminate H_2 or, if MNU is the substrate, undergo CH_2 insertion followed by reductive elimination. In the case of ENU, insertion of methylcarbene into the Rh–H bond and subsequent formation of ethane may be obviated by a relatively rapid 1,2-hydrogen atom shift in free CH_3CH forming ethylene which is observed in the product gases. The reaction chemistry thus described is summarized in the Scheme I. The factors influencing the relative ease of carbene insertion into the binuclear hydride formed, and the relative propensity of these systems to form isocyanate complexes vs. bridging carbene complexes are under continuing study.

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Registry No. 1, 74507-92-9; 2, 77010-18-5; 3, 74507-93-0; 4, 81616-70-8; MNU, 684-93-5; ENU, 759-73-9.

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Mild, Low-Pressure Carbonylation of (π-Allyl)palladium Complexes†

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Summary: **In the presence of carboxylic acid anions, the normally difficult carbonylation of (π-allyl)palladium complexes can be achieved quantitatively at low pressure and temperature, thereby providing a new low-pressure route to β,γ-unsaturated esters from olefins. A (π-allyl)carbalkoxypalladium complex is proposed to be a key intermediate in this reaction.**

Organic synthesis via (π-allyl)palladium complexes has attracted much attention in recent years.[1,2] Pd(II) salts provide activation of the allylic position of an olefin, thus forming the basis for a variety of allylic alkylation reactions.[2] Carbonylation of (π-allyl)palladium complexes, although still a useful reaction, has found much less application in organic synthesis since it requires high CO pressure, high temperature, is very slow, and results in modest yields of carbonylation products.[3,4] Difficulties

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† Contribution No. 3001.

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