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A Transition-Metal-Based Method for 1,2-Diamination of Alkenes. Synthesis of Cobalt Dinitrosoalkanes from Alkenes, Nitric Oxide, and (η^5-Cyclopentadienyl)nitrosylcobalt Dimer and Their Reduction to Primary Vicinal Diamines

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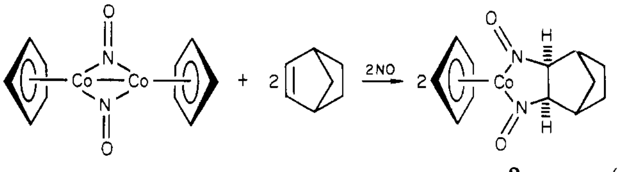
Unstrained alkenes of the general structure $R_1R_2C{=}CR_3R_4$ (R_1, R_2, R_3, R_4 = alkyl, hydrogen) react with $[\eta^5\text{-}C_5H_5CoNO]_2$/NO to produce cobalt 1,2-dinitrosoalkane complexes having the general formula $(\eta^5\text{-}C_5H_5)(R_1R_2R_3R_4C_2N_2O_2)Co$ in high yield. Many of these complexes are stable enough to isolate and characterize fully; less stable complexes can be generated successfully in situ. The most stable complex was derived from the tetrasubstituted alkene 2,3-dimethyl-2-butene. Two different cobalt dinitrosoalkane complexes (**5** and **6**) result from (*E*)- and (*Z*)-3-methyl-2-pentene, respectively, establishing that the reaction occurs stereospecifically. The dinitrosoalkane ligands are inert to displacement by CO and phosphines. Reduction of these complexes with $LiAlH_4$ occurs readily at −78 to −50 °C. Overall, this constitutes a general method for conversion of alkenes into primary vicinal aliphatic diamines. The stereospecificity of reduction depends on the substituent geometry of the dinitrosoalkane ligand. The major diastereomer produced by reduction of the complex derived from (*E*)-3-hexene was *d*,*l*-3,4-diaminohexane. Thus, the major diamine is the one formed via syn addition of two NH_2 groups to the alkene. An increase in stereospecificity by a factor of 2.5 for the production of *d*,*l*-3,4-diaminohexane was realized by first reducing its dinitrosoalkane precursor with $(i\text{-Bu})_2AlH$ followed by $LiAlH_4$.

Introduction

Chemical methods for oxidizing olefins to cis diols using reagents like $KMnO_4$ and OsO_4 have been known for some time. The analogous transformation to produce vicinal diamines has been far more difficult to achieve. A two-step sequence may be envisioned involving halogenation of an olefin followed by displacement with ammonia. However, this reaction is limited to compounds containing two and three carbon units. Higher homologues principally undergo elimination.[1] The first stereospecific synthesis of vicinal aliphatic diamines was worked out by Swift and Swern.[1] Their procedure was based on several reactions whose stereochemistry was well established. The use of transition metals has recently resulted in a few successful one-pot procedures.[2] They suffer from the limitation of only being able to make N-alkylated secondary or tertiary amines and often do not work well with heavily substituted alkenes. Thus there is a need for new and more general 1,2-diamination procedures, especially those which might provide primary diamines.

In 1968, Brunner reported that $CpCo(CO)_2$ (Cp = η^5-C_5H_5) reacts with nitric oxide gas to form a dimer, $[CpCoNO]_2$.[3] A few years later, he and Loskot discovered that this dimer reacted further with NO in the presence of strained bicyclo[2.2.1]hept-2-enes to form cobalt dinitrosoalkane complexes according to the stoichiometry in eq 1.[4] The cis-exo structure, initially determined by ^1H NMR spectroscopy, was later confirmed by a single-crystal X-ray diffraction study of the complex obtained from norbornadiene.[5]



1 **2** (1)

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[1] A brief summary covering the synthesis of vicinal aliphatic diamines up to 1967 can be found in: Swift, G.; Swern, D. *J. Org. Chem.* **1967**, *32*, 511.

[2] See, for example: (a) Backvall, J. *Tetrahedron Lett.* **1978**, *2*, 163. (b) Chong, A.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420. (c) Aranda, V. G.; Barluenga, J.; Aznar, F. *Synthesis* **1974**, 504. (d) Barluenga, J.; Alonso-cires, L.; Asencio, G. *Ibid.* **1979**, 962.

[3] Brunner, H. *J. Organomet. Chem.* **1968**, *12*, 517.

[4] (a) Brunner, H.; Loskot, S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 515. (b) *J. Organomet. Chem.* **1973**, *61*, 401.

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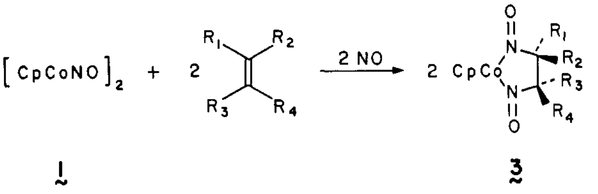
Scheme I



The potential of this reaction has been noted in several reviews.[6] This is an unusual organometallic transformation because it involves reaction at two ligand atoms, rather than at the metal. From a practical point of view, it forms two new carbon–nitrogen bonds in a cis relationship. The possibility that this might be a general reaction represents a potentially very useful transformation from readily available olefin starting materials. There were two immediate obstacles however: (1) it was not clear from Brunner's studies whether simple, unstrained olefins could be made to ract with dimer 1 in good yield; (2) it was uncertain whether methods could be found for cleaving the cobalt–nitrogen linkage in order to release the newly functionalized organic fragment.

Recently, we reported our preliminary results on reaction of simple olefins with this system and the subsequent reduction of the products of this reaction into primary vicinal aliphatic diamines.[7] This paper provides the full details of the synthesis and stereochemistry of cobalt dinitrosoalkane formation from $[CpCoNO]_2$/NO and olefins and describes factors affecting the stability of these complexes. We also discuss other approaches to cleaving the cobalt–nitrogen bond and elaborate on the reduction of dinitrosoalkane complexes to diamines. A detailed mechanistic investigation of the reaction between $[CpCoNO]_2$/NO and olefins has also been carried out and will be published separately.[8]

Results and Discussion

Synthesis of Cobalt Dinitrosoalkane Complexes. Although Brunner and Loskot reported that only dinitrosoalkane complexes derived from norbornene-type olefins could be formed in good yield, they noted that ethylene and cyclohexene also reacted.[4a] However, their reaction products could not be obtained pure. Upon reinvestigating this reaction, we found that in addition to cyclohexene, a variety of simple aliphatic olefins could be converted into dinitrosoalkane ligands yielding cobalt complexes of the type 3 (Scheme I).

Our initial goal was to optimize reaction conditions. Using cyclohexene and following the published procedure for the norbornene-type olefins,[4b] we found that after less than 20-min reaction with NO gas, all of the cobalt dimer 1 had been consumed but 80% of the olefin was still unreacted. The solution contained some dinitrosoalkane complex as determined from its IR spectrum (ν_{NO} = 1420 (m) and 1375 (s) cm^{-1} in THF), but the majority of the cobalt species were present as a brown, intractable precipitate. This indicated that there was a large difference in reactivity between unstrained olefins and bicyclo[2.2.1]hept-2-enes.

As a working hypothesis, we guessed that the reaction involved the mechanism illustrated in Scheme II. We judged that simple olefins did not trap the proposed intermediate $CpCo(NO)_2$ fast enough to compete successfully with decomposition pathways. We reasoned that increasing the molar concentration of both reactants should increase this trapping rate and thus improve the yield of product. Experiments corroborate this prediction. When the reaction was run by using 0.2 M $[CpCoNO]_2$ and 0.4 M olefin, good conversion of olefin and cobalt dimer into cobalt dinitrosoalkane took place. If the olefin is readily available, it is also advisable to use it in excess (~5×) since this further optimizes the yield based on cobalt.

Scheme II

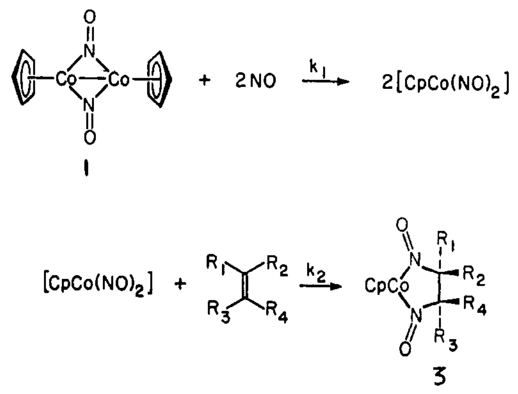
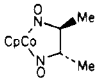
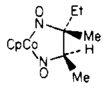
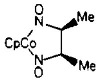
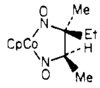
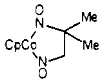
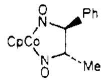
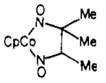
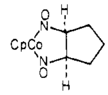
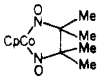
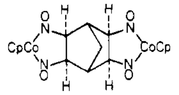


Table I. Yield of Isolated Cobalt Dinitrosoalkanes Prepared from Olefins and $[CpCoNO]_2$/NO

cobalt dinitrosoalkane complex	isolated yield,[a] %	cobalt dinitrosoalkane complex	isolated yield,[a] %
	84		82
	63		86
	62		92
	84		73
	79		68

[a] Yield is based on cobalt.

The (dinitrosonorbornyl)cobalt complexes described by Brunner are exceptionally stable to air and heat. For example, 2 can withstand refluxing in benzene and only slowly decomposes in refluxing toluene. By contrast, solutions of most dinitrosoalkane complexes formed from unstrained olefins decompose at room temperature giving an uncharacterized brown precipitate. Therefore, as a further modification of Brunner's procedure, we have found that cooling the reaction to 0 °C provides the best compromise between maximizing the rate of complex formation and minimizing competitive thermal decomposition pathways.

Table I shows the yields (not optimized) of isolated and fully characterized cobalt dinitrosoalkane complexes obtained by using these procedures. We found that by using exactly 1 equiv of olefin and dimer 1, both double bonds

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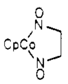
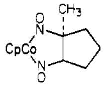
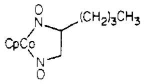
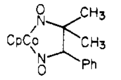
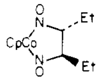
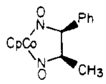
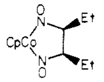
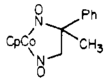
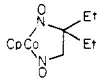
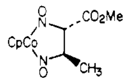
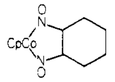
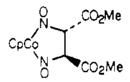
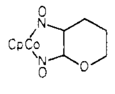
(5) Evrard, G.; Thomas, R.; Davis, B.; Bernal, I. *J. Organomet. Chem.* **1977**, *124*, 59.

(6) Connelly, N. G. *Inorg. Chim. Acta Rev.* **1972**, 47. (b) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53.

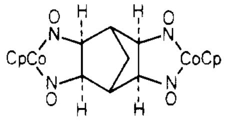
(7) Becker, P.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5676.

(8) Becker, P.; Bergman, R. G. *J. Am. Chem. Soc.*, in press.

Table II. In Situ Formed Cobalt Dinitrosoalkanes and Their NO Stretching Frequencies in THF

cobalt dinitroso-alkane complex	NO stretching frequency, cm^{-1}	cobalt dinitroso-alkane complex	NO stretching frequency, cm^{-1}
	1428, 1363		1427, 1375 1360
	1427, 1370		1430, 1387 1365
	1427, 1362		1428, 1378 1354
	1418, 1370		1433, 1375 1361
	1425, 1365		1430, 1378 1362
	1425, 1378		1435, 1365
	1435, 1388 1365		

in norbornadiene could be functionalized, producing complex 4.[9] These materials were all air stable when crys-



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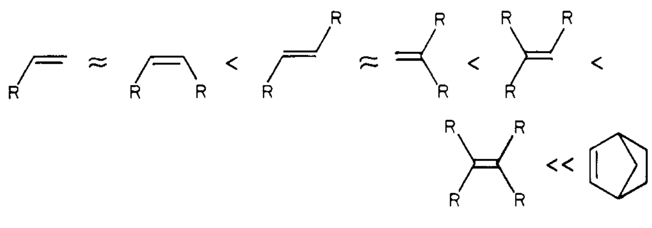
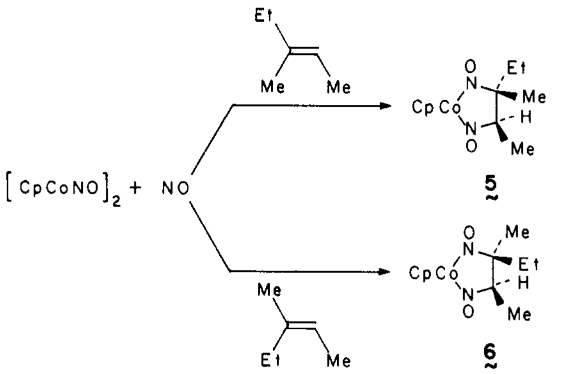
talline. Table II lists the IR stretching frequencies for complexes that were generated in situ. In general, their solutions are easily manipulated since they were unaffected by brief exposure to atmospheric oxygen. The most commonly encountered difficulty was the thermal instability of some of the complexes.

The drawing below shows a series of olefins arranged in order of increasing stability of the dinitrosoalkane complexes 3 that they form.



Except for the norbornyl and cyclopentyl complexes, stability is adversely affected by the number of hydrogens α to the nitroso group. It also depends on their geometry. Cis hydrogens have a detrimental effect, whereas complexes with geminal hydrogens can often be isolated and characterized. Further substitution of hydrogen by alkyl groups or introduction of strain leads to readily isolable products. If the thermal decomposition of these complexes

Scheme III



involves removal or intramolecular migration of α-hydrogens, as the stability series above suggests, then there should be a deuterium isotope effect on the rate of decomposition. This was verified when the complex 7 synthesized from (*Z*)-3,4-dideuterio-3-hexene proved to be qualitatively much more stable than its protio analogue. Similarly, replacement of hydrogen by CH_3 gave a complex that showed no tendency to undergo decomposition in solution at room temperature. This was the most stable cobalt dinitrosoalkane we prepared from an unstrained olefin. Like the norbornyl complexes, solutions of this compound also exhibited no tendency to react with atmospheric oxygen. Some of the other thermally stable dinitrosoalkane complexes appear to be slightly, but unpredicitably, air-sensitive while in solution.

Stereochemistry of Cobalt Dinitrosoalkane Complexes. We wished to determine whether the formation of cobalt dinitrosoalkanes was stereospecific—that is, whether *E* and *Z* olefins gave isomerically pure dinitrosoalkane complexes. Brunner had already established that nitrosylation of norbornene-type olefins occurred in a cis fashion.[4,5] Because the ridgidity of the norbornene skeleton enforces this result, it cannot automatically be generalized to include acyclic olefins. Rigorously determining the stereochemistry of acyclic olefin nitrosylation first required finding a system in which both isomeric dinitrosoalkane complexes would be stable enough to isolate and characterize by standard methods. Secondly, these complexes had to be distinguishable by ^1H NMR spectroscopy so that analysis of the reaction stereochemistry would be possible. These conditions could not be fulfilled by using the complexes obtained from (*E*)- and (*Z*)-2-butene since the resonances in their NMR spectra overlapped.

The trisubstituted olefins (*E*)- and (*Z*)-3-methyl-2-pentene proved to be the substrates of choice. When reacted separately with $[CpCoNO]_2$ and NO in CH_2Cl_2, they yielded the stable, isomeric cobalt dinitrosoalkanes 5 and 6, respectively (Scheme III). Both compounds were slightly air-sensitive and had to be recrystallized under a nitrogen atmosphere. These complexes could be stored in the solid state at −40 °C for extended periods of time. In benzene solution at room temperature, neither showed any sign of decomposition. However, dissolution of 6 for an extended time resulted in slow conversion to an intractable brown powder.

Fortunately, the ^1H NMR resonances of complexes 5 and 6 are well separated (see Experimental Section) allowing us to verify that each olefin produced a different product and proving that the reaction is completely stereospecific within the limits of detectability (±2%). We can infer that the addition occurs in a cis fashion since the diamines produced by $LiAlH_4$ reduction are those formed by cis

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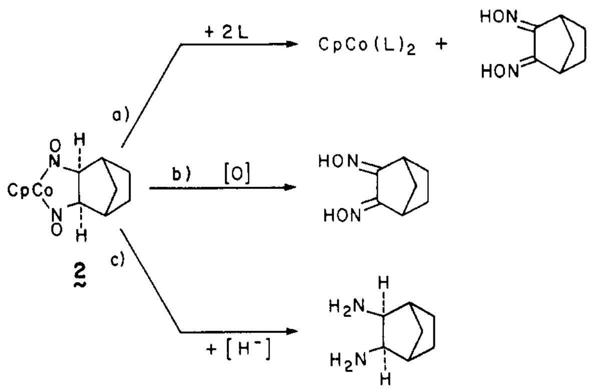
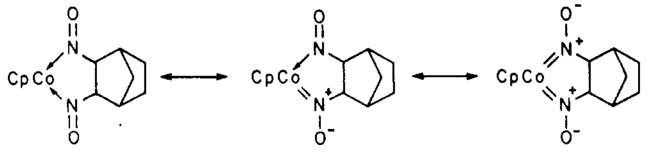
[9] Brunner reported[4b] that the reaction stopped after only one double bond had reacted in norbornadiene. This conclusion probably resulted from the low solubility of the monofunctionalized product that crystallizes out of solution unless the reaction is run under dilute conditions.

Scheme IV



Scheme V



2a **2b** **2c**

attachment of two NH_2 groups to the olefin precursor (vide infra).

Reaction of Cobalt Dinitrosoalkanes with CO and Phosphines. Having been successful at finding the proper conditions under which cobalt dinitrosoalkanes could be made from simple aliphatic olefins, we focused our efforts on devising methods to remove the dinitrosoalkane ligand from cobalt. Such a process was of interest because it would allow isolation of organic compounds containing new vicinal carbon–nitrogen bonds.

Scheme IV outlines three routes designed to solve this problem. The first is simple ligand displacement (path a). If the dinitrosoalkane ligand is bound to cobalt through a dative bond as in resonance structure **2a** (Scheme V), then it should undergo displacement reactions with donor ligands like CO and phosphines. The expected products would be the well-known $CpCo(L)_2$ complexes along with the free dinitrosoalkane that might tautomerize to its dioxime form.[10] Such a scheme has the attraction that, in the case where L = CO, $CpCo(CO)_2$ could be nitrosylated to regenerate $[CpCoNO]_2$.

We used the air-stable norbornyl complex **2** as a model compound to examine this possibility. Unfortunately, the dinitrosoalkane ligand maintains a surprisingly tenacious grip on the cobalt atom—**2** could not be made to react with CO even at 850 psi and 80 °C in benzene solution. Similarly, reaction of **2** with the more nucleophilic ligand PMe_3 in benzene did not occur at room temperature. At 80 °C this mixture decomposed, but 2,3-dioximinonorbornane was not present in the mixture as judged by comparison of its R_f (TLC on SiO_2) and ^1H NMR spectrum (in THF-d_8) with those of an authentic, independently prepared sample. Other phosphines tried include PF_3 and PPh_3: these gave no reaction except decomposition upon heating to 110 °C.

These experiments suggest that **2a** does not provide a complete description of the bonding between cobalt and the dinitrosoalkane ligand. Resonance structures **2b** and **2c** (Scheme V) propose that in addition to the dative interaction, there is also some π back-bonding which occurs between cobalt and the nitroso group. The net result is a stronger cobalt–nitrogen bond that could explain why ligand dissociation is so difficult. Supporting evidence for back-bonding can be found in the slightly elongated NO bond lenths calculated in the crystal structure of the norbornadiene derived complex.[5] The N–O bond (1.252 Å) is shorter than singly bonded organic nitroxides (1.27–1.29 Å)[11] but slightly lengthened relative to doubly bonded nitroso compounds like monomeric 4-iodonitrosobenzene (1.24 Å) and coordinated 2-methyl-2-nitrosopropane (1.21 Å)[12] in $PtCl_2(t\text{-}BuNO)_2$. The NO stretching frequency (1357 cm^{-1}) also occurs in a region between that of free di-*tert*-butyl nitroxide (1343 cm^{-1}) and free (1546 cm^{-1}) as well as coordinated 2-methyl-2-nitrosopropane (1555 cm^{-1}) in $PtCl_2(t\text{-}BuNO)_2$.[12] Bernal used these data to propose that the dinitrosoalkane ligand may actually be a coordinated dinitroxide.[5]

Oxidation of Cobalt Dinitrosoalkanes. Since the cobalt–nitroso bond appeared to be inert to ligand displacement reaction, we tried oxidizing these complexes (path b, Scheme IV). It is well established that while a metal may tightly bind its ligands changing the oxidation state can make those same ligands become extremely labile.[13] We found that dinitrosonorbornane complex **2** readily reacted with 2 equiv of iodine in -THF-d_8. The ^1H NMR spectrum revealed that the resonance for **2** at 4.86 (s) ppm had been quantitatively replaced by a new one at 5.94 (s, 5 H) ppm. There was also a broad resonance downfield at 12.11 (s, 2 H) ppm, characteristic of oxime protons. The IR spectrum showed only a weak, broad band at 1420 cm^{-1}. Subjecting this mixture to chromatography on silica gel did not give 2,3-dioximinonorbornane and only decomposed the material. This suggested that the dinitrosoalkane was still complexed to cobalt.

Removal of solvent produced an oil that could not be purified further. However, treatment of this compound with 2 equiv of PPh_3 resulted in another immediate reaction. The organometallic product was readily identified as $CpCo(PPh_3)I_2$ by its singlet resonances at 5.11 (5 H) ppm and the solution's dark green color. One equivalent of $P(O)Ph_3$ was also produced. The alkyl resonances belonging to the norbornane fragment were now greatly broadened, suggesting that it was paramagnetic. Consistent with this, no dioxime could be detected by ^1H NMR spectroscopy or by TLC on silica gel. However hydrolysis of the iodinated THF solution with saturated aqueous $NaCl/Na_2S_2O_3$, gave 2,3-dioximinonorbornane in 60% yield after chromatography on silica gel. Unfortunately, this procedure failed to yield any 1,2-cyclohexanedione dioxime from the cobalt dinitrosocyclohexane complex (generated in situ from cyclohexene and **1**), and we cannot therefore consider this a general procedure.

Hydride Reduction of Cobalt Dinitrosoalkanes to 1,2-Diamines. Metal hydride reduction of the dinitrosoalkane ligands proved to be the method of choice for removal of these ligands from cobalt. Formally, the reaction involves four hydride equivalents to reduce two nitroso functionalities to primary amino groups that retain their

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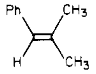
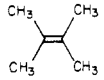
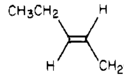
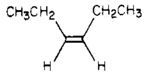
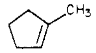
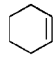
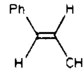
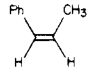
[10] Since no studies have been done on vicinal dinitrosoalkanes, we cannot be certain that both nitroso groups will behave independently and tautomerize to oxime. In fact, even simple alkylnitroso → oxime transformation may have a substantial energy barrier in the absence of acid or base catalysis. For example, the E_a for tautomerization of nitrosomethane in the gas phase is 35 kcal/mol while nitrosocyclohexane dimerizes much more rapidly than it tautomerizes. For a review containing references on these studies see: Gowenlock, B. G.; Luttke, W. *Q. Rev., Chem. Soc.* **1958**, *12*, 321.

[11] Taken from Table 9 of ref 5.

[12] Bond distances and stretching frequencies taken from data and references in: Mansuy, D.; Dreme, M.; Chottard, J. C.; Guilhem, J. *J. Organomet. Chem.* **1978**, *161*, 207.

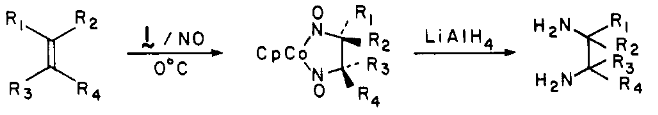
[13] For a recent study of change in reactivity as a function of metal oxidation state for alkyl iron complexes, see: Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155.

Table III. Conversion of Alkenes to 1,2-Diamines Using $[CpCoNO]_2$

alkene	alkene, nmol	$[CpCoNO]_2$, nmol	reactn time,^{a} min	yield, %	ratio of diastereomers, %
	3.33	2.48	60^b	80	4/6/90
	3.35	2.50	40	70	30/70
	3.35	2.50	120	78^d	
	3.35	2.50	85	66^d	
	2.90	2.20	75 $(120)^c$	61 $(80)^c$	90/10
	3.30	2.49	150 $(140)^c$	43 $(62)^c$	34/66
$C_4H_9CH{=}CH_2$	3.33	2.48	60	79	
	3.39	2.50	70	65	20/80
	3.39	2.50	120	47	32/68
	3.35	2.53	90	90	85/15
	3.30	2.47	120	74^d	28/72

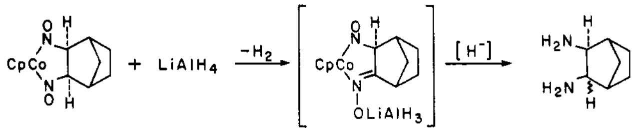
[a] Refers to time required for formation of adduct 3 from 1 and alkene. [b] This reaction not monitored by GC; reaction time not optimized in this case. [c] Yield in parentheses obtained by adding a second 2.5 mmol of dimer 3 after 30 min. [d] Yield of product isolated after conversion to cyclic urea derivative.

Scheme VI



3

Scheme VII



2

cis stereochemical relationship (path c, Scheme IV). When pure cis-exo complex 2 was allowed to react with $LiAlH_4$ in THF at −78 °C, a mixture of isomeric 2,3-diaminobicyclo[2.2.1]heptanes could be isolated in 80% yield. GC analysis showed that the cis-exo diamine made up 90% of the mixture and a 3:2 ratio of the other two isomers (not assigned) made up the remaining 10%. We did not attempt to isolate the organometallic products of $LiAlH_4$ reduction prior to hydrolysis.

To examine the generality of this reduction, a series of olefins was reacted with $[CpCoNO]_2$ (1) and NO in THF at 0 °C to form the corresponding cobalt dinitrosoalkanes, and these complexes were reduced in situ with $LiAlH_4$ at −78 °C (Scheme VI). The isolated yields and relative amounts of diastereomeric diamines produced are displayed in Table III. The yields (based on olefin) range from fair for cyclohexene to excellent for *trans-β*-methylstyrene. Except for norbornene, the diastereomer ratio is poorer for cis- than for trans-disubstituted olefins. In each case, the major diamine produced is the one obtained by syn addition of two NH_2 groups to the olefin. This was established by identifying the major product of the (*E*)-3-hexene reaction as *d,l*-3,4-diaminohexane—a known compound whose stereochemical assignment was made by Swift and Swern.[1,14] In general, the stereoselectivity of the $LiAlH_4$ reduction and the diamine yield appear to parallel the thermal stability of the corresponding dinitrosoalkane complex. For example, in the case of *E* and *Z* olefins, the *E* olefin reacts faster, producing the more thermally stable cobalt complex, whose reduction by $LiAlH_4$ is in turn more selective.

Since we have evidence that the cobalt dinitrosoalkane complexes 3 are formed with high stereospecificity, the production of diastereomeric diamines must be due to epimerization during the $LiAlH_4$ reduction. One possible mechanism for the loss of stereochemistry involves base-cataylzed nitroso-to-oxime tautomerization. As Scheme VII depicts, $LiAlH_4$ may react with the acidic α-nitroso protons, liberating hydrogen gas and forming an oxime salt. Since reduction of the resulting carbon–nitrogen double bond can occur from either the exo or endo side, all three possible diastereomeric diamines are formed. By this

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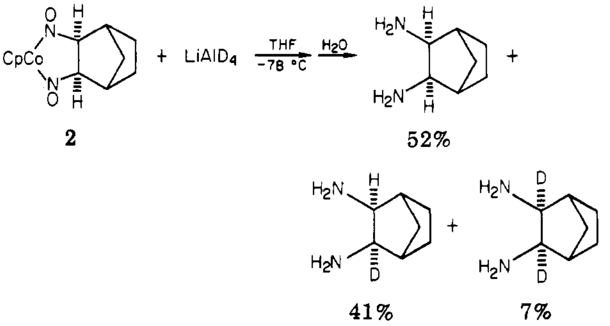
(14) According to ref 1, the dihydrochloride salt of the *d,l* diamine melts at 298–300 °C while the meso isomer's salt melts at 263–266 °C. The dihydrochloride salt of the major product from the (*E*)-3-hexene reaction (which was first separated from the minor isomer by preparative VPC) had a melting point of 297–299 °C, establishing that it was the *d,l* isomer.

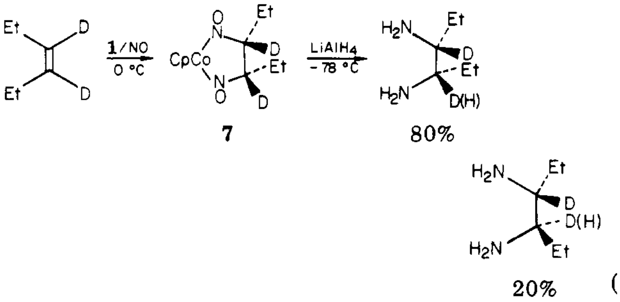
mechanism, reduction of 2 with $LiAlD_4$ would be expected to incorporate deuterium at the α-amino position. As eq 2 shows, mass spectral analysis of the cis-exo diamine from



(2)

this reaction found a substantial amount of deuterium present. ^1H NMR spectroscopy confirmed that it was located entirely at the α-amino position. The two minor isomers, analyzed as a mixture, showed somewhat increased amounts of d_2 and decreased amounts of d_0 diamines. This indicated that at least part of the conversion to diamine (even in the cis-exo case) involves tautomerization of both nitroso functionalities during reduction.

Another prediction of this base-induced tautomerization is that it ought to be retarded by deuterium substitution at the α-nitroso position. As a result, there should be an increase in the overall stereoselectivity of the reduction. To test this hypothesis, (*Z*)-3,4-dideuterio-3-hexene (>93% deuterium incorporation) was allowed to react with dimer 1 and NO, forming α,α′-dideuteriodinitrosoalkane complex 7 (eq 3). This was reduced in situ with $LiAlH_4$, followed by the standard workup procedure. GC analysis of the diamine product showed a twofold increase in stereoselectivity relative to the undeuterated case (2/1 to 4/1 ratio of diastereomers). ^1H NMR spectroscopy also showed only a 23% decrease in deuterium content of the α-amino position, consistent with less of the base-induced mechanism than in the protiodinitrosoalkane/$LiAlD_4$ reaction (eq 2).



(3)

These results suggested that use of a more hindered and/or less basic reducing agent might improve stereoselectivity in these reductions. Diisobutylaluminum hydride (DiBAL) reacted rapidly with undeutereated complex 7 at −78 °C but failed to yield any diamine on workup. However, when the DiBAL reduction was followed by the usual $LiAlH_4$ reduction at −50 °C, the diamines were obtained. GC analysis showed that the diastereomer ratio had increased to 5/1. Thus, this modification improved the stereoselectivity by a factor of 2.5. Encouraged by these findings, we are investigating other hydride reducing systems aimed at maximizing stereoselectivity of diamine synthesis from olefins.

Conclusions

We have found that cobalt dinitrosoalkanes can be synthesized in good yield from unstrained aliphatic olefins using Brunner's system ($[CpCoNO]_2$/NO]. Many of these complexes undergo thermal decomposition while in solution at room temperature, but are stable for extended time periods at 0 °C. Increasing the reactant concentrations improves conversion to products and minimizes reaction time and therefore product decomposition. Stereochemical studies have shown that the addition occurs stereospecifically in a syn fashion.

The utility of this organometallic system for organic synthesis is best realized by $LiAlH_4$ reduction of the dinitrosoalkane ligands to vicinal diamines. This represents the first general method for the direct transformation of olefins into *primary* 1,2-diamines. The reaction shows some stereoselectivity that improves with the stability of the cobalt dinitrosoalkane precursor. Because our system reacts well with even trialkyl- and tetraalkyl-substituted olefins, its scope is broader than previously developed diamination reagents.[2]

Experimental Section

General Data. All manipulations of oxygen or water sensitive materials were conducted under a prescrubbed recirculating atmosphere of nitrogen in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 MHz spectrometer or a 200 or a 250 MHz high-field Fourier tranform instrument. The high-field system consisted of a Cryomagnetics Inc. magnet, Nicolet Model 1180 data collection systems, and electronics assembled by Mr. Rudi Nunlist of U. C. Berkeley. Chemical shifts are reported relative to tetramethylsilane.

Infrared (IR) spectra were recorded on a Perkin-Elmer 283 grating spectrometer using either NaCl solution cells of KBr ground pellets. Mass spectroscopic (MS analyses were obtained on an AFI MS-1 spectrometer interfaced with a Finnigan 2300 data system. Elemental analyses were obtained from U. C. Berkeley analytical facility. Melting points were recorded on a Thomas Hoover capillary melting point apparatus.

Tetrahydrofuran, diethyl ether, dimethoxyethane, benzene, and toluene were dried with sodium benzophenone ketyl and distilled under nitrogen. Methylene chloride was distilled from CaH_2 under nitrogen. Hexane was purified by 2 × 12 h of stirring over 98% sulfuric acid followed by 2 × 6 h of stirring over saturated $KMnO_4$ in 10% sulfuric acid. It was then sequentially washed with water, saturated Na_2CO_3, and water, dried over $MgSO_4$, filtered, and distilled under nitrogen from *n*-butyllithium.

Nitric oxide gas was used directly as purchased from Matheson. $CpCo(CO)_2$ was prepared according to the literature procedure.[15] All olefins were degassed with nitrogen for 3 min prior to use. Unless otherwise stated, all reagents were used without further purification.

Preparation of $[CpCoNO]_2$ (1). The dimeric $[CpCoNO]_2$ was synthesized via Brunner's procedure[3] with minor modifications for scale-up and purification.

A 2-L three-neck round-bottom flask equipped with magnetic stir bar, gas-tight stopcock, rubber septum, and an air-tight gas inlet tube was charged with 79.8 g (0.43 mol) of 97% $CpCo(CO)_2$[16] and 1200 mL of hexane under a positive pressure of dry nitrogen. NO gas was allowed to bubble slowly[17] through the red solution, which gradually darkened and deposited precipitate as the reaction proceeded. Occasionally the NO bubbler became clogged which

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(15) Rausch, M. D.; et al. *J. Org. Chem.* **1970**, *35*, 3888.

(16) The 3% impurity is dicyclopentadiene that codistills with $CpCo(CO)_2$ during its purification. If pure $CpCo(CO)_2$ is desired, it may be obtained by passing the distillate down a long silica gel column eluted with hexanes. Under these conditions dicyclopentadiene with R_f 0.8 elutes first and $CpCo(CO)_2$ (R_f 0.25) follows as a dark red band. Solvent evaporation of this fraction yields pure $CpCo(CO)_2$.

(17) It is important that NO gas be bubbled slowly during this reaction because rapid bubbling results in formation of an insoluble reddish brown precipitate that contains no $[CpCoNO]_2$. Apparently, this reaction is complicated by the fact that the product also reacts with NO, even in the solid state.

required stopping the reaction to unplug the apparatus. The disappearance of $CpCo(CO)_2$ was conveniently monitored by TLC on silica gel (hexane eluent). After ~12 h, the reaction was complete. The solution was purged of NO by bubbling dry nitrogen through it for ~5 min. The reddish brown precipitate was collected on a medium frit and washed with 200 mL of hexane. In a drybox or nitrogen-filled glovebag, the solid was dissolved in 600 mL of benzene and filtered to remove insoluble material. To purify $[CpCoNO]_2$ from the dicyclopentadiene adduct, this benzene solution was passed down a 650-mL (7.5 × 9 cm) medium frit filter slurry packed with silica gel in hexane. More benzene was poured through this frit column until all the $[CpCoNO]_2$ had been eluted as a dark green solution. The red dicyclopentadiene adduct remains immobilized on silica gel under these conditions. Evaporation of solvent gave 38.7 g (0.13 mol, 60% yield) of pure $[CpCoNO]_2$ as black crystals: IR (KBr) 1583 (m), 1525 (s) cm^{-1}, (THF) 1592 (m), 1540 (s) cm^{-1}, (C_6H_6) 1590 (m), 1534 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.53 (s, 10 H), (THF δ 4.83 (s, 10 H) [lit.[3] IR (KBr) 1585 (s), 1525 (ss, br) cm^{-1}; ^1H NMR (C_6D_6) δ 4.77 (s, 10 H)].

This material is best stored under nitrogen to prevent surface oxidation, even though as a solid it is air-stable for extended periods of time. In solution, this dimer reacts slowly with oxygen as evidenced by deposition of precipitate.

Preparation of $CpCo(C_6H_{12}N_2O_2)$ from 1 and 2,3-Dimethyl-2-butene. In a drybox, a three-neck 25-mL pear-shaped flask equipped with magnetic stir bar, rubber septum, Teflon stopper, and air-tight gas inlet tube was charged with 0.915 g (3 mmol) of $[CpCoNO]_2$ (1) and 10 mL of CH_2Cl_2. The apparatus was taken to a hood and placed under positive pressure of dry nitrogen. A 3.5-g (42-mmol) sample of 2,3-dimethyl-2-butene was deoxygenated by bubbling nitrogen through it for 3 min and then added to the mixture via syringe. NO gas was slowly bubbled through the mixture. The disappearance of 1 was monitored by TLC on silica gel (benzene eluent). After ~1 h, the resulting dark red solution was filtered through a medium frit and flash evaporated to remove unreacted olefin, leaving a black solid. This was recrystallized from CH_2Cl_2/Et_2O/hexane (1/1/1) at −20 °C to give 1.26 g (4.7 mmol, 78% yield) of analytically pure black crystals: mp 150–155 °C dec; IR (THF) 1433 (m), 1426 (m), 1390 (s), 1360 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.74 (s, 5 H), 0.93 (s, 12 H), (THF-d_8 δ 4.84 (s, 5 H), 1.09 (s, 12 H); MS (70 eV), m/e 268 (M^+). Anal. Calcd for $C_{11}H_{17}N_2O_2Co$: C, 49.26; H, 6.39; N, 10.44; Co, 22.0. Found: C, 49.36; H, 6.52; N, 10.46; Co, 21.9.

Preparation of $CpCo(C_5H_{10}N_2O_2)$ from 1 and 2-Methyl-2-butene. In a manner analogous to the preparation of the 2,3-dimethyl-2-butene adduct, 0.920 g (3.0 mmol) of 1 was mixed with 3.3 g (47 mmol) of 2-methyl-2-butene in 10 mL of CH_2Cl_2. After the solution was cooled to 0 °C, NO was bubbled through the mixture for 75 min, the solution filtered, solvent evaporated, and the residue recrystallized from CH_2Cl_2/Et_2O/hexane (1/1/1) at −60 °C to give 1.27 g (5.0 mmol, 84% yeild) of analytically pure black crystals: mp 135–140 °C dec; IR (THF) 1430 (m), 1389 (s), 1372 (m), 1357 (s), 1334 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.75 (s, 5 H), 2.43 (q, $J_{H,H}$ = 6.6 Hz, 1 H), 1.05 (s, 3 H), 1.01 (d, $J_{H,H}$ = 6.6 Hz, 3 H), 0.98 (s, 3 H); MS (70 eV), m/e 254 (M^+). Anal. Calcd for $C_{10}H_{15}N_2O_2Co$: C, 47.25; H, 5.95; N, 11.02; Co, 23.2. Found: C, 47.26; H, 5.96; N, 11.02; Co, 22.9.

Preparation of $CpCo(C_4H_8N_2O_2)$ from 1 and Isobutylene. In a drybox, a three-neck 25-mL pear-shaped flask equipped with stir bar, two air-tight gas inlet tubes, and a Teflon stopcock was charged with 0.932 g (3.0 mmol) of 1 and 10 mL of CH_2Cl_2. The apparatus was taken to a hood, placed under positive pressure of dry nitrogen, and cooled in an ice bath at 0 °C. Between 5 and 10 mL of isobutylene was ocndensed into the solution through one of the gas inlet tubes. NO was then bubbled through the solution for 70 min. After filtration and solvent evaporation, the residue was chromatographed in the air on silica gel (4 × 20 cm) using 5% Et_2O/95% CH_2Cl_2 as eluent. The product eluted as a dark red band with the solvent front. The solution was concentrated to 10 mL, 20 mL of Et_2O was added, and cooling to −60 °C resulted in 0.90 g (3.7 mmol, 62% yield) of analytically pure black crystals: mp >230 °C dec; IR (KBr) 1420 (m), 1361 (m), 1351 (s), 1310 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.73 (s, 5 H), 2.47 (s, 2 H), 1.01 (s, 6 H); MS (70 eV), m/e 240 (M^+). Anal. Calcd for $C_9H_{13}N_2O_2Co$: C, 45.01; H, 5.46; N, 11.67; Co, 24.5. Found: C, 45.03; H, 5.46; N, 11.72; Co, 24.0.

Preparation of $CpCo((E)\text{-}C_4H_8N_2O_2)$ from 1 and (*E*)-2-Butene. In a manner analogous to the preparation of the isobutylene adduct, 5–10 mL of (*E*)-2-butene was condensed into a three-neck 25-mL pear-shaped flask containing 0.985 g (3.2 mmol) of 1 was in 10 mL of CH_2Cl_2 at 0 °C. NO was bubbled through the solution for 50 min. Filtration, evaporation of solvent, and recrystallization of the residue from 7 mL of CH_2Cl_2/35 mL of Et_2O at −60 °C gave 1.30 g (5.4 mmol, 84% yield) of analytically pure black crystals: mp 100–120 °C dec; IR (THF) 1428 (m), 1372 (s), 1357 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.75 (s, 5 H), 2.31 (m, 2 H), 1.04 (d, $J_{H,H}$ = 6.3 Hz, 6 H); MS (70 eV) m/e 240 (M^+). Anal. Calcd for $C_9H_{13}N_2O_2Co$: C, 45.01; H, 5.46; N, 11.67; Co, 24.5. Found: C, 44.94; H, 5.37; N, 11.55; Co, 24.8.

Preparation of $CpCo((Z)\text{-}C_4H_8N_2O_2)$ from 1 and (*Z*)-2-Butene. In a manner analogous to the preparation of the isobutylene adduct, 5–10 mL of (*Z*)-2-butene was condensed into a three-neck 25-mL pear-shaped flask containing 0.510 g (1.6 mmol) of 1 in 10 mL of CH_2Cl_2 at 0 °C. NO was bubbled through the solution for 50 min. Filtration, evaporation of solvent at 0 °C, and recrystallization of the residue from 5 mL of CH_2Cl_2/10 mL of Et_2O/5 mL of hexane at −60 °C gave 0.492 g (2.0 mmol, 63% yield) of analytically pure black crystals. This material is quite thermally sensitive, and storage at −40 °C is recommended: mp 60–65 °C dec; IR (KBr) 1422 (m), 1382 (s), 1350 (s) cm^{-1}; ^1H NMR ($CDCl_3$ at 0 °C δ 4.93 (s, 5 H), 3.04 (m, 2 H), 1.17 (d, $J_{H,H}$ = 6.2 Hz, 6 H); MS (70 eV), m/e 240 (M^+). Anal. Calcd for $C_9H_{13}N_2O_2Co$: C, 45.01; H, 5.46; N, 11.67; Co, 24.5. Found: C, 45.07; H, 5.47; N, 11.58; Co, 25.2.

Preparation of $CpCo((E)\text{-}C_6H_{12}N_2O_2)$ (5) from 1 and (*E*)-3-Methyl-2-pentene. In a manner analogous to the preparation of the 2,3-dimethyl-2-butene adduct, 0.870 g (2.8 mmol) of 1 was combined with 3.75 g (44 mmol) of (*E*)-3-methyl-2-pentene in 10 mL of CH_2Cl_2 and reacted with NO for 60 min. After filtration and evaportion of solvent, the residue was taken into a drybox where it was recrystallized from 7 mL of toluene/10 mL of Et_2O at −40 °C to give 1.25 g (4.7 mmol, 82% yield) of analytically pure black crystals: mp (N_2) 77–78 °C; IR (hexane) 1430 (m), 1388 (br, s), 1359 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.74 (s, 5 H), 2.67 (q, $J_{H,H}$ = 6.9 Hz, 1 H), 1.49 (m, 1 H), 1.26 (m, 1 H, 0.97 (d, $J_{H,H}$ = 7.5 Hz, 3 H); MS (70 eV), m/e 268 (M^+). Anal. Calcd for $C_{11}H_{17}N_2O_2Co$: C, 49.26; H, 6.39; N, 10.44; Co, 22.0. Found: C, 49.50; H, 6.35; N, 10.40; Co, 21.8.

Preparation of $CpCo((Z)\text{-}C_5H_{10}N_2O_2)$ (6) from 1 and (*Z*)-3-Methyl-2-pentene. In a manner analogous to the preparation of the 2,3-dimethyl-2-butene adduct, 1.03 g (3.3 mmol) of 1 was combined with 3.75 g (44 mmol) of (*Z*-3-methyl-2-pentene in 10 mL of CH_2Cl_2 and reacted with NO for 60 min. After filtration and evaporation of solvent, the residue was taken into a drybox where it was recrystallized from 10 mL of toluene/10 mL of Et_2O at −40 °C to give 1.7 g (6.3 mmol, 95% yield) of analytically pure 6 as black crystals: mp (N_2) 70 °C dec; IR (THF) 1430 (m), 1380 (br, s), 1361 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.74 (s, 5 H), 2.35 (q, $J_{H,H}$ = 6.8 Hz, 1 H), 1.1–1.4 (m, 2 H), 0.96 (d, $J_{H,H}$ = 6.8 Hz, 3 H), 0.94 (s, 3 H), 0.58 (t, $J_{H,H}$ = 7.4 Hz, 3 H); MS (70 eV) m/e 268 (M^+). Anal. Calcd for $C_{11}H_{17}N_2O_2Co$: C, 49.26; H, 6.39; N, 10.44; Co, 22.0. Found: C, 49.28: H, 6.51; N, 10.58; Co, 21.7.

Preparation of $CpCo((E)\text{-}C_9H_{10}N_2O_2)$ from 1 and (*E*)-1-Phenyl-1-propene. In a manner analogous to the preparation of the 2,3-dimethyl-2-butene adduct, 0.620 g (2.0 mmol) of 1 was combined with 2.37 g (20 mmol) of (*E*)-1-phenyl-1-propene in 10 mL of CH_2Cl_2 and reacted with NO at room temperature for 40 min. After filtration and evaporation of solvent, the excess olefin was removed by rapid trituration with pentane. The residue was taken into a drybox where it was redissolved in 8 mL of Et_2O/3 mL of CH_2Cl_2 and filtered. Addition of 10 mL of pentane followed by cooling to −40 °C resulted in 1.13 g (3.7 mmol, 92% yield) of analytically pure black crystals: mp (N_2) 95–100 °C; IR (THF) 1427 (m), 1370 (s), 1358 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 7.02 (m, 5 H), 4.69 (s, 5 H), 3.48 (d, $J_{H,H}$ = 2.90 Hz, 1 H), 2.99 (d of q, $J_{H,H}$ = 2.90 and 6.76 Hz, 1 H), 1.05 (d, $J_{H,H}$ = 6.76 Hz, 3 H); MS (70 eV), m/e 302 (M^+). Anal. Calcd for $C_{14}H_{15}N_2O_2Co$: C, 55.64; H, 5.00; N, 9.27; Co, 19.5. Found: C, 55.66; H, 5.03; N, 9.18; Co, 19.6.

Preparation of $CpCo(C_5H_8N_2O_2)$ from 1 and Cyclopentene. In a manner analogous to the preparation of the 2,3-dimethyl-

2-butene adduct, 0.230 g (0.75 mmol) of 1 was combined with 0.214 g (3.1 mmol) of cyclopentene in 5 mL of CH_2Cl_2 and reacted with NO at 0 °C (because of the volatility of cyclopentene) for 40 min. after evaporation of solvent, the residue was chromatographed on silica gel (2.4 × 22 cm) using 5% Et_2O/95% CH_2Cl_2 to elute the product as a dark red band. Evaporation of solvent gave 0.276 g (1.1 mmol, 73% yield) of analytically pure black crystals: mp 110 °C dec; IR (KBr) 1415 (m), 1353 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.94 (s, 5 H), 3.20 (m, 2 H), 1.2–1.4 (m, 6 H); MS (70 eV), *m/e* 252 (M^+). Anal. Calcd for $C_{10}H_{13}N_2O_2Co$: C, 47.63; H, 5.20; N, 11.11; Co, 23.4. Found: C, 47.01; H, 5.18; N, 11.15; Co, 22.8.

Preparation of $(CpCo)_2(C_7H_8N_4O_4)$ (4) from 1 and Norbornadiene. In a manner analogous to the preparation of the 2,3-dimethyl-2-butene adduct, 0.818 g (3.0 mmol) of 1 was combined with 0.265 g (2.9 mmol) of norbornadiene in 55 mL of CH_2Cl_2 and reacted with NO for 40 min. The resulting product precipitated and was filtered from the reaction solution. The red-brown solid was dissolved in 150 mL of hot $CHCl_3$, filtered, and allowed to cool to −20 °C. Filtration gave 0.730 g (2.0 mmol, 68% yield) of analytically pure fluffy red-brown crystals. This compound is highly insoluble in most organic solvents: mp 220–240 °C dec; IR (THF) 1425 (m), 1358 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 4.61 (s, 10 H), 3.17 (m, 2 H), 2.14 (br s, 4 H), 1.18 (br s, 2 H); MS (70 eV), *m/e* 460 (M^+). Anal. Calcd for $C_{17}H_{18}N_4O_4Co_2$: C, 44.37; H, 3.94; N, 12.17; CO, 25.6. Found: C, 44.65; H, 3.95; N, 12.19; Co, 25.3.

Reaction of 2 with Iodine and PPh_3. The proton chemical shifts found in this reaction in THF-d_8 have already been described in the text. The following preparative experiment was carried out by using protio THF.

In a drybox, a 50-mL round-bottom flask equipped with magnetic stir bar was charged with 47 mg (0.17 mmol) of 2 in 9 mL of THF. To this stirred red solution was added 90 mg (0.35 mmol) of I_2 as a solid. The reaction immediately turned olive brown. After 15 min, 10 mg (0.38 mmol) of PPh_3 was added as a solid. The solution became bright green, characteristic of the formation of $CpCo(PPh_3)I_2$. A TLC on silica gel (30% Et_2O/70% THF eluent) showed $CpCo(PPh_3)I_2$ (R_f 0.77), a colorless UV-active organic product (R_f 0.55), and a brown spot that streaked at the origin. There was no spot possessing an R_f 0.70 identical with that for 2,3-dioximinonorbornane. Chromatography of the reaction residue on silica gel using 55% THF/45% Et_2O as eluent afforded a quantitative yield of $CpCo(PPh_3)I_2$ (108 mg, 0.17 mmol) and 48 mg of a crystalline colorless solid identified as $(O)PPh_3$ (0.17 mmol, 100% yield) by comparison of its ^1H NMR spectrum with that of a known sample (Aldrich). Monitoring this reaction with infrared spectroscopy shows no definitive or strongly absorbing N–O stretches that could help characterize the iodinated intermediate or the norbornyl nitroso fragment after treatment with PPh_3.

2,3-Dioximinonorbornane. A 250-mL round-bottom flask equipped with a stir bar was charged with 7.0 g (100 mmol) of hydroxylamine hydrochloride dissolved in 24 mL of water at 0 °C. To this stirred solution was added 66 g (100 mmol) of 85% KOH dissolved in 16 mL of water, also cooled to 0 °C. A 5.0-g (40.2-mmol) sample of 2,3-dioxonorbornane[18] was added as a solid, and the mixture was covered and allowed to stir for 1 h at 0 °C. During this time, most of the yellow diketone had dissolved and a white suspension had formed. After 15 h at room temperature, a white precipitate was collected on a Buchner funnel, stirred over 50 mL of H_2O for 5 min to remove any possible salts, and refiltered, giving a light pink solid (color due to traces of Fe^{2+} complex). The initial aqueous filtrate from the reaction was concentrated under vacuum to a solid residue and then stirred over 150 mL of THF. The THF solution was filtered and evaporated under vacuum also producing a pink solid. The combined pink solids (5.46 g, 35 mmol, 88% crude yield) were recrystallized from boiling water in two crops, giving 3.96 g (26 mmol, 64% yield) of analytically pure white crystals: mp 173–174 °C; IR (KBr) 3385 (br s), 1634 (w) cm^{-1}; ^1H NMR (THF-d_8) δ 9.94 (s, 2 H), 3.58 (m, 2 H, accurate integration not possible due to overlap with solvent signal), 1.72 (m, 2 H, accurate integration not possible due to overlap with solvent signal), 1.44 (m, 4 H); MS (70 eV), *m/e* 154 (M^+). Anal. Calcd for $C_7H_{10}N_2O_2$: C, 54.53; H, 6.54; N, 18.17. Found: C, 54.27; H, 6.59; N, 17.96.

The sharp melting point and single oxime proton resonance observed suggest that only one isomer is present and are consistent with its tentative assignment as the trans,trans 1,2-dioxime.

Preparation of 2,3-Dioximinonorbornane from 2. A 100-mL round-bottom flask equipped with a stir bar was charged with 194 mg (0.70 mmol) of 2 and 30 mL of THF. To this stirred mixture was added a solution of 372 mg (1.46 mmol) of I_2 dissolved in 10 mL of THF. The solution immediately became olive brown. TLC on silica gel (20% hexane/80% Et_2O) showed that 2 had completely reacted in 6 min. The mixture was poured into a 125-mL separatory funnel containing 50 mL of saturated aqueous $Na_2S_2O_3$/NaCl solution. After the funnel was shaken vigorously for 1 min, the aqueous layer became dark blue while the organic layer was dark brown. The THF layer was dried over $MgSO_4$, filtered, and concentrated under vacuum to a dark semi-solidified oil. Column chromatography on silica gel (2.2 × 27 cm) using 20% hexane/80% Et_2O as eluent gave 66 mg (0.12 mmol, 61% yield) of 2,3-dioximinonorbornane as a pure white solid. Since the ^1H NMR and IR spectra of this material were found to be identical with those of an independently synthesized sample, we presume that it also only contains the trans,trans-1,2-dioxime isomer.

Preparation of 1,2-Diamines from Olefins via $LiAlH_4$ Reduction. The following is a general procedure applicable to all olefins employed. The actual amounts of various reagents used as well as the reaction times required to form the cobalt dinitrosoalkanes are listed in Table III.

A three-neck 25-mL pear-shaped flask equipped with stir bar, rubber septum, air-tight gas inlet tube, and dry ice condenser (for the more volatile olefins) was charged with ~2.5 mmol of $[CpCoNO]_2$ (1) under a positive pressure of argon. Freshly distilled THF (10 mL) and 3.3–3.4 mmol of olefin, deoxygenated by bubbling nitrogen through it for 3 min, were added via syringe. The resulting dark green solution was cooled to 0 °C and the condenser (if necessary) cooled to −78 °C. After argon had purged the solution for 5–10 min, nitric oxide gas was bubbled very slowly (<3 mL/min) through the mixture.[17] The reaction is best monitored by following the disappearance of 1 using TLC on silica gel (benzene or 5% Et_2O/35% CH_2Cl_2/60% hexane as eluent).

When all of 1 had reacted,[19] the red solution was purged of excess NO by bubbling argon through it for 5 min, diluted to a total volume of 20 mL with THF (added via cannula), and cooled to −65 °C. This was added dropwise via cannula over a 10–15-min period to a 250-mL three-neck round-bottom flask, fitted with a reflux condenser and rubber septum and containing ~40 mmol of $LiAlH_4$ slurried in 50 mL of THF at −70 °C under a nitrogen atmosphere. The reaction mixture became dark green as the temperature increased (usually between −55 and −60 °C). The initial reaction vessel was rinsed with 20 mL of THF, and its contents were added in the same manner to the $LiAlH_4$ mixture. After being warmed to room temperature, the solution was left to stir overnight and/or refluxed for 1–3 h, giving a black suspension. The excess $LiAlH_4$ was quenched at −60 °C according to the method of Fieser and Fieser.[20,21] After the mixture was warmed to room temperature and stirred for 4 h, it was filtered and the precipitate was washed with 2 × 30 mL of THF. The THF solution was dried over K_2CO_3, filtered, and evaporated under vacuum to give an oil (usually dark yellow in color). Bulb to bulb distillation at <5 μm and room temperature[22] into a

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(18) Prepared according to the literature method of: Alder, K.; et al. *Justus Liebigs Ann. Chem.* **1955**, *593*, 23–35.

(19) Usually there is between 5 and 15% of unreacted olefin still present when using unstrained alkenes. This is why addition of another equivalent of $[CpCoNO]_2$ midway through the reaction helps to increase the conversion of olefin and the yield of diamine (see Table III, footnote c).

(20) For every *x* g of $LiAlH_4$ used, add dropwise *x* mL of H_2O, *x* mL of 15% NaOH, and 3*x* mL of H_2O in that order. See: L. Fieser and M. Fieser, "Reagents for Organic Synthesis"; Wiley-Interscience: New York, 1967; Vol. 1, p 584.

(21) We have found that quenching $LiAlH_4$ by using the Fieser and Fieser technique results in an excess of H_2O so that large amounts of K_2CO_3 were required to dry the solution. This problem can be circumvented by limiting the final dropwise addition of H_2O to 2.7*x* instead of 3*x*.

(22) For diamines containing more than seven carbons, distillation was carried out at elevated temperatures.

liquid-nitrogen-cooled trap provided >95% pure diamine. Many of the diamines react rapidly with atmospheric CO_2. As a result, well-sealed containers under nitrogen atmosphere or conversion to the dihydrochloride salt are recommended for long term storage. Analytically pure samples were obtained by preparative GC on a 33 ft. × $^1/_4$ in. column packed with 10% DC710 on Chrom W containing 5% KOH on 60-80 mesh.[23] This column was also used to analyze the ratios of diamine diastereomers present in the purified products.

The analytical and spectroscopic data for each of the diamines are given below. Ratios of stereoisomers for each case are given in Table III.

2,3-Diaminonorbornane: IR (neat) 3380 (m), 3300 (m), 1610 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 2.79 (s, 2 H), 1.96 (m, 2 H), 1.73–0.93 (m, 6 H); MS (70 eV), *m/e* 126 (M$^+$). Anal. Calcd for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.38; H, 10.96; N, 21.92.

2,3-Diaminocyclopentane: IR (neat) 3360 (m), 3280 (m), 1600 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 3.10–2.40 (m, 2 H), 2.05–0.95 (m, 6 H). Anal. Calcd for $C_5H_{12}N_2$: C, 59.95; H, 12.08; N, 27.97. Found: C, 59.73; H, 11.98; N, 27.89.

1,2-Diamino-1-phenyl-2-methylpropane: IR (neat) 3360 (m), 3290 (m), 1600 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 7.25 (s, 5 H), 3.60 (s, 1 H), 1.00 (s, 6 H). Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.12; H, 9.83; N, 17.06. Found: C, 73.11; H, 9.66; N, 17.14.

2,3-Diamino-2,3-dimethyl-2-butane: IR (neat) 3360 (m), 3300 (m), 1590 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.03 (br s, 16 H). This material was a white paste. To facilitate characterization, it was converted to the solid urea derivative by using selenium metal and CO/O_2 in THF:[24] mp 202–204 °C; IR (KBr) 3200 (br m), 1700 (m) cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.31 (s, 12 H). Anal. Calcd for $C_7H_{14}N_2O$: C, 59.13; H, 9.92; N, 19.70. Found: C, 59.19; H, 9.69; N, 17.79.

3,4-Diaminohexane (from (*E*)-3-hexene): IR (neat) 3365 (m), 3290 (m), 1595 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 2.56 (m, 2 H), 1.76–1.16 (m, 4 H), 0.96 (t, $J_{H,H}$ = 6.9 Hz, 6 H). Anal. Calcd for $C_6H_{16}N_2$: C, 62.01; H, 13.88; N, 24.11. Found: C, 62.06; H, 13.72; N, 23.97.

***d,l*-3,4-Diaminohexane Dihydrochloride.** The major diamine isomer obtained from (*E*)-3-hexene starting material was separated from the minor product by preparative GC on the above-mentioned column. This material was dissolved in ether and converted to the dihydrochloride by bubbling a stream of dry hydrogen chloride through the solution. The white solid that precipitated was recrystallized from ether/95% ethanol: mp 293–297 °C; IR (KBr) 2900 (s, br), 2020 (m), 1610 (s), 1523 (s) cm^{-1}; ^{1}H NMR (D_2O) δ 3.41 (m, 2 H), 1.59 (m, 4 H), 0.89 (t, $J_{H,H}$ = 7.4 Hz, 6 H) [lit.[1] mp 298–300 °C; IR 2800, 2000, 1620, 1520 cm^{-1}].

Since the pure meso diamine dihydrochloride isomer is reported[1] to melt at a lower temperature (263–266 °C), we can safely assign the *d,l* structure to our diamine dihydrochloride.

3,4-Diaminohexane (from (*Z*)-3-hexene): IR (neat) 3380 (m), 3300 (m), 1600 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 2.54 (m, 2 H), 1.70–1.16 (m, 4 H), 0.93 (t, $J_{H,H}$ = 6.9 Hz, 6 H). Anal. Calcd for $C_6H_{16}N_2$: C, 62.01; H, 13.88; N, 24.11. Found: C, 61.99; H, 13.61; N, 23.88.

1,2-Diaminohexane: IR (neat): 3360 (m), 3290 (m), 1595 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 2.83–2.30 (m, 3 H), 1.53–1.16 (m, 6 H), 0.97 (t, $J_{H,H}$ = 7.5 Hz, 3 H). Anal. Calcd for $C_6H_{16}N_2$: C, 62.01; H, 13.88; N, 24.11. Found: C, 61.88; H, 13.73; N, 24.02.

1,2-Diaminocyclohexane: IR (neat) 3360 (m), 3290 (m), 1595 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 2.82 (m, 2 H), 2.10–1.20 (m, 8 H). The IR and ^{1}H NMR spectra from this diamine mixture contained the same stretching frequencies and proton resonances found in a commercial sample (Aldrich). However, the intensities were somewhat different since the commercial sample contained a 2/1 (*d,l*/meso) diamine ratio while the our method yielded a 1/2 ratio.

1,2-Diamino-1-phenylpropane (from (*E*)-1-phenylpropene): IR (neat) 3370 (m), 3290 (m), 1600 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 7.27 (s, 5 H), 3.52 (d, $J_{H,H}$ = 6.9 Hz, 1 H), 2.91 (quin, $J_{H,H}$ = 6.5 Hz, 1 H), 1.06 (d, $J_{H,H}$ = 6.5 Hz, 3 H, minor isomer 15%), 0.86 (d, $J_{H,H}$ = 6.5 Hz, 3 H, major isomer 85%). Anal. Calcd for $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.37; H, 9.14; N, 18.36.

1,2-Diamino-1-phenylpropane (from (*Z*)-1-phenylpropene): IR (neat) 3360 (m), 3300 (m), 1610 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 7.27 (s, 5 H), 3.52 (d, $J_{H,H}$ = 6.9 Hz, 1 H), 2.91 (quin, $J_{H,H}$ = 6.5 Hz, 1 H), 1.06 (d, $J_{H,H}$ = 6.5 Hz, 3 H, major isomer 72%), 0.86 (d, $J_{H,H}$ = 6.5 Hz, 3 H, minor isomer 28%). Anal. Calcd for $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.61; H, 9.36; N, 18.46.

1,2-Diamino-1-methylcyclopentane. IR (neat) 3360 (m), 3280 (m), 1600 (m) cm^{-1}; ^{1}H NMR (D_2O) δ 2.75 (m, 1 H), 2.10–1.27 (m, 6 H), 1.17 (s, 3 H, major isomer 75%), 107 (s, 3 H, minor isomer 25%). Anal. Calcd for $C_6H_{14}N_2$: C, 63.11; H, 12.36; N, 24.53. Found: C, 62.92; H, 12.25; N, 24.58.

Preparation of (*Z*)-3,4-Dideuterio-3-hexene. This compound was prepared with >93% D incorporation (by ^{1}H NMR) at the olefinic position using the literature procedure[25] starting from 3-hexyne and BD_3. It was separated from starting material by preparative VPC on a 20 ft × $^3/_8$ in. column packed with 30% Carbowax 20 M on Chrom P: ^{1}H NMR ($CDCl_3$) δ 1.92 (q, $J_{H,H}$ = 7.5 Hz, 4 H), 0.85 (t, $J_{H,H}$ = 7.5 Hz, 6 H).

Preparation of 3,4-Diaminohexane from DiBAL Reduction. In a manner analogous to the $LiAlH_4$ procedure, 0.630 g (2.7 mmol) of 1 was combined with 0.675 g (7.2 mmol) of (*Z*)-3-hexene in 15 mL of Et_2O and reacted with NO at 0 °C for 40 min. After dilution and cooling to −78 °C, this solution was added dropwise to a 100-mL round-bottom flask equipped with a stir bar and rubber septum that was charged with 2.8 g (20 mmol) of diisobutylaluminum hydride (DiBAL) in 30 mL of Et_2O at −78 °C. The cobalt dinitrosoalkane reacted immediately producing a green solution. After being stirred for 1.5 h, this mixture was added to a 250-mL three-neck round bottom flask fitted with reflux condenser, rubber septum, and stir bar and charged with 1.1 g (29 mmol) of $LiAlH_4$ suspended in 70 mL of THF at −50 °C. After being stirred 1 h, the mixture was brought to reflux (40 °C) for 2 h and then left to stir overnight at room temperature. Cooling to 0 °C followed by the usual quenching procedure[20] and workup gave 220 mg (35% yield): an additional amount (ca. 20–40%) was accidentally lost during the initial reduction. GC analysis showed a 5/1 ratio (increased from 2/1 in the $LiAlH_4$ reduction) of diastereomeric diamines.

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Registry No. **1**, 51862-20-5; **2**, 51262-48-7; **3** ($R^1 = R^2 = R^3 = R^4 = CH_3$), 82640-85-5; **3** ($R^1 = R^2 = R^3 = CH_3$; $R^4 = H$), 84849-63-8; **3** ($R^1 = R^2 = CH_3$; $R^3 = R^4 = H$), 82640-83-3; **3** ($R^1 = R^4 = CH_3$; $R^2 = R^3 = H$), 84849-64-9; **3** ($R^1 = R^3 = CH_3$; $R^2 = R^4 = H$), 84893-99-2; **3** ($R^1 = Ph$; $R^2 = R^3 = H$; $R^4 = CH_3$), 82640-81-1; **3** ($R^1, R^3 = (CH_2)_3$; $R^2 = R^4 = H$), 84849-66-1; **3** ($R^1 = R^2 = R^3 = R^4 = H$), 84849-68-3; **3** ($R^1 = (CH_2)_3CH_3$; $R^2 = R^3 = R^4 = H$), 82692-23-7; **3** ($R^1 = R^4 = Et$; $R^2 = R^3 = H$), 82660-73-9; **3** ($R^1 = R^3 = Et$; $R^2 = R^4 = H$), 82640-80-0; **3** ($R^1 = R^2 = Et$; $R^3 = R^4 = H$), 84849-69-4; **3** ($R^1, R^3 = (CH_2)_4$; $R^2 = R^4 = H$), 84849-70-7; **3** ($R^1, R^3 = (CH_2)_3O$; $R^2 = R^4 = H$), 84849-71-8; **3** ($R^1 = CH_3$; $R^2, R^4 = (CH_2)_3$; $R^3 = H$), 84849-72-9; **3** ($R^1 = R^2 = CH_3$; $R^3 = Ph$; $R^4 = H$), 82640-84-4; **3** ($R^1 = R^3 = H$; $R^2 = Ph$; $R^4 = CH_3$), 82660-75-1; **3** ($R^1 = CH_3$; $R^2 = Ph$; $R^3 = R^4 = H$), 84849-73-0; **3** ($R^1 = R^4 = H$; $R^2 = CO_2Me$; $R^3 = CH_3$), 84849-74-1; **3** ($R^1 = R^4 = H$; $R^2 = R^3 = CO_2Me$), 84849-75-2; **4**, 84849-67-2; **5**, 84849-65-0; **6**, 84894-00-8; $CpCo(CO)_2$, 12078-25-0; $CpCo(PPh_3)I_2$, 12194-27-3; (*E*)-3-methyl-2-pentene, 616-12-6; (*Z*)-3-methyl-2-pentene, 922-62-3; (*E*)-1-phenyl-1-propene, 873-66-5; *trans*,-*trans*-2,3-dioximinonorbornane, 84849-58-1; 2,3-dioxonorbornane, 6236-71-1; *endo*,*exo*-2,3-diaminonorbornane, 45657-74-7; *endo*,-*endo*-2,3-diaminonorbornane, 74779-33-2; *exo*,*exo*-2,3-diaminonorbornane, 45657-75-8; *trans*-1,2-diaminocyclopentane, 3145-88-8; *cis*-1,2-diaminocyclopentane, 40535-45-3; 1,2-diamino-1-phenyl-2-methylpropane, 74745-63-4; 2,3-diamino-2,3-dimethylbutane, 20485-44-3; *d,l*-3,4-diaminohexane, 82644-73-3; *meso*-3,4-diaminohexane, 74745-64-5; *d,l*-3,4-diaminohexane dihydrochloride,

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[23] See: Smith, E. D.; Radford, R. D. *Anal. Chem.* **1961**, *33*, 1160.

[24] We used a high yield method developed by Kondo, Kiyoshi; et al. *Synthesis* **1979**, 735.

[25] Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 1512.

84849-59-2; 1,2-diaminohexane, 13880-27-8; *cis*-1,2-diamino-1-methylcyclopentane, 84849-60-5; *trans*-1,2-diamino-1-methylcyclopentane, 84849-61-6; *cis*-1,2-diaminocyclohexane, 1436-59-5; *trans*-1,2-diaminocyclohexane, 1121-22-8; *d,l*-1,2-diamino-1-phenylpropane, 84849-62-7; *meso*-1,2-diamino-1-phenylpropane, 74745-66-7; (*Z*)-3,4-dideuterio-3-hexene, 76596-51-5; 2-methyl-1-phenyl-1-propene, 768-49-0; (*E*)-3-hexene, 13269-52-8; (*Z*)-3-hexene, 7642-09-3; 1-methylcyclopentene, 693-89-0; 1-phenyl-1-propene, 873-66-5; 2,3-dimethyl-2-butene, 563-79-1; 2-methyl-2-butene, 513-35-9; isobutylene, 115-11-7; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; cyclopentene, 142-29-0; norbornadiene, 121-46-0; triphenylphosphine oxide, 791-28-6; hydroxylamine hydrochloride, 5470-11-1; 1-hexene, 592-41-6; cyclohexene, 110-83-8.

Synthesis and Characterization of Organoaluminum Compounds Containing the (Trimethylsilyl)methyl Substituent, Al(CH$_2$SiMe$_3$)$_2$Br, Al(CH$_2$SiMe$_3$)$_2$H, and (Me$_3$SiCH$_2$)$_2$AlPPh$_2$, and a Reinvestigation of the Chemistry of Me$_2$AlPPh$_2$ and Et$_2$AlPPh$_2$

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The new amphoteric ligand (Me$_3$SiCH$_2$)$_2$AlPPh$_2$ has been prepared from the reactions of either Al(CH$_2$SiMe$_3$)$_3$ or Al(CH$_2$SiMe$_3$)$_2$H with PPh$_2$H or Al(CH$_2$SiMe$_3$)$_2$Br with KPPh$_2$ and fully characterized by analysis, cryoscopic molecular weight measurements, and IR and ^{1}H NMR data. This aluminum phosphide is unique as it exists as a monomer–dimer equilibrium mixture in benzene solution. The syntheses and characterization of the new compounds Al(CH$_2$SiMe$_3$)$_2$H and Al(CH$_2$SiMe$_3$)$_2$Br are also described. Since the chemistry of aluminum phosphides as amphoteric ligands is of interest, the behavior of (Me$_3$SiCH$_2$)$_2$AlPPh$_2$, (Me$_2$AlPPh$_2$)$_2$, and (Et$_2$AlPPh$_2$)$_2$ toward common solvents Et$_2$O, THF, and CH$_3$CN was investigated. The aluminum phosphides readily cleave THF and reduce the triple bond of CH$_3$CN at room temperature. However, neither THF nor Et$_2$O form isolable adducts with aluminum phosphides. The unusual melting point behavior of aluminum phosphides is also discussed.

Introduction

The synthesis and characterization of Cr(CO)$_5$[PPh$_2$Al(CH$_2$SiMe$_3$)$_2$·NMe$_3$][1] has been described recently. This compound serves as a model for compounds in which a diphenylphosphide group bridges a transition metal and a main-group element moiety. Alternatively, this new compound may be considered to be a transition-metal derivative of an organoaluminum phosphide, an amphoteric ligand. As part of this research effort, the chemistry of amphoteric ligands is of interest and consequently we have extended, reinvestigated, and in some cases reassessed the chemistry of several organoaluminum diphenylphosphides.

Organoaluminum diphenylphosphides with methyl,[2] ethyl,[3] and aryl[4] substituents have been prepared from triorganoaluminum compounds and PPh$_2$H by elimination reactions. The compounds R$_2$AlPPh$_2$ exist as dimers in benzene solution and are believed to have four-membered aluminum–phosphorus rings in analogy with similar compounds containing other group 3 and group 5 atoms.[2-4] The four-membered rings reportedly can be disrupted by reaction with various Lewis bases to form adducts of formula Ph$_2$PAlR$_2$·base.[2-4] However, no NMR or X-ray structural data have been reported to support the proposed structures of dimers or of their adducts. The lack of such data prompted us to undertake a reinvestigation of the properties and reaction chemistry of Me$_2$AlPPh$_2$ and Et$_2$AlPPh$_2$. The results of our initial attempts to synthesize M(CO)$_5$PPh$_2$AlR$_2$ compounds defined the need for a more soluble organoaluminum diphenylphosphide. Our previous experience[5,6] had indicated that the (trimethylsilyl)methyl ligand enhanced the solubility of its compounds in hydrocarbon solvents. Thus, we prepared (Me$_3$SiCH$_2$)$_2$AlPPh$_2$ from Al(CH$_2$SiMe$_3$)$_3$, Al(CH$_2$SiMe$_3$)$_2$Br, and Al(CH$_2$SiMe$_3$)$_2$H in order to define the best and most useful route. Our new convenient synthesis of Al(CH$_2$SiMe$_3$)$_3$ has been reported.[7] From this parent compound, the preparations of Al(CH$_2$SiMe$_3$)$_2$Br and Al(CH$_2$SiMe$_3$)$_2$H have been accomplished. In this paper we also report the properties of the adducts of R$_3$AlPPh$_2$H (R = Me, Et, CH$_2$SiMe$_3$) and the chemistry of organoaluminum diphenylphosphides toward ethers (THF and Et$_2$O) and CH$_3$CN.

Experimental Section

Handling procedures, solvent purification, and spectra were as previously described.[1] All molecular weights were measured cryoscopically in benzene solution.[1] Moles of hydrolyzable alkyl groups or hydrogens bound to aluminum were determined by measuring the gas (PVT) evolved upon acid hydrolysis from a weighed sample of compound[1] (mol). Attempts to analyze for aluminum via an EDTA titration[2] in the presence of phosphorus were unsuccessful. Immediately prior to its use AlMe$_3$ was vacuum distilled. AlEt$_3$ was obtained from a commercial 25% solution in hexane by removal of hexane by vacuum distillation. The compound AlMe$_2$H was obtained from the reaction of AlMe$_3$ and LiAlH$_4$[8] and was purified by vacuum distillation. The reagents

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