is 97%, O_2 evolution is not observed, and $O{=}PPh_3$ is produced stoichiometrically. An oxidizing equivalent ($^1/_2O_2$) is produced in these reactions since only two electrons (from **1**) of the four needed (eq 1) have been provided.

We also find that nitric oxide (NO(g)) reacts with Cu(I) complexes to give copper–nitrosyl intermediates, which convert to oxo–dicopper(II) complexes and N_2O (Scheme II). These reactions further demonstrate (cf. Scheme I) the use of Cu^{II} ion (rather than H^+) to help drive oxo-transfer reactions, trapping O^{2-} and producing Cu–O–Cu complexes. Thus, exposure of **1** to NO(g) at −80 °C in CH_2Cl_2 gives an unstable purple-brown solution (λ_{max} = 380 nm). Standing or warming produces N_2O (96%) and oxo complex **3** (55%, isolated). A similar reactivity is observed for **4**; the unstable intermediate (λ_{max} = 358 nm) decomposes to give a 56% yield of N_2O and oxo complex **5**.[15] The reaction of NO(g) with mononuclear Cu(I) complex **6** is more interesting because a deep purple −80 °C stable intermediate (**7**) forms in EtCN (Scheme II). This arises from the stoichiometric addition of 1 NO per copper ion complex **6** (manometry in EtCN at −80 °C; 1.09 ± 0.11 NO/Cu, three trials). Direct evidence for a copper–nitrosyl species was obtained by using FT-IR spectroscopy via in situ low-temperature monitoring.[16] A 1460-cm^{-1} absorption is assigned to ν_{NO} on the basis of its shifting to 1446 cm^{-1} when labeled ^{15}NO (99%) is used. This particularly low energy ν_{NO}[1a] value and the observed EPR silence of these purple solutions suggest a dinuclear $Cu^{II}–(NO^-)_2–Cu^{II}$ formulation for intermediate **7**,[17] perhaps facilitating the N–N coupling reaction to give the N_2O product (98%) observed. A dinuclear oxo–dicopper(II) complex (**8**) (78%) is again formed.[18]

Thus, we have shown that copper ion complexes can mediate N–N coupling reactions starting with NO_2^- *or* NO(g). The latter reactions appear to proceed via dinitrosyl intermediates, as is observed in the chemistry of other transition metals.[1b,19] The present study provides the first example of a reaction of a metal–nitrosyl compound with nitrite (Scheme I);[1b] N_2O generation makes this reaction notably reminiscent of Averill and Tiejde's proposal for N_2O production in the iron and copper enzymes.[3,20] We have also provided the first authenticated example (by IR spectroscopy) of a {Cu–NO} complex (i.e., dinuclear **7**) generated from a Cu(I) precursor and NO(g).

On the basis of the copper-mediated coupling of NO(g) we observe here (i.e., Scheme II), we suggest an alternate possible reaction pathway for N_2O production by protein nitrite reductases, not previously considered. Free NO(g)[2-5] may be formed via a prior one-electron reduction and dehydration of NO_2^-, and release. Attack of NO(g) on a separately formed enzyme (type 2)[9] {Cu–NO} intermediate[3] could proceed through a dinitrosyl {$Cu–(NO)_2$} intermediate,[1b,19] leading to N–N coupling. Additional reduction (via type 1 Cu?)[9] and protonation of a putative $Cu–(N_2O_2)$ intermediate[3] would complete the stoichiometric reaction (eq 1), giving nitrous oxide and water. In our model system, the chemistry is mediated and an extra electron supplied by the second copper ion, the latter being a role probably reserved for type 1 copper in the protein.

Further studies will deal with other aspects of $Cu–NO_x$ chemistry and mechanistic investigations of the systems described here.

Acknowledgment. We are grateful to the National Institutes of Health for support of this research.

Note Added in Proof. Recent studies with *A. cycloclastes* nitrite reductase[3d] are consistent with a NO(g) rebound mechanism, which may well be analogous to the chemistry suggested here.

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[15] $[Cu_2(N4)O](PF_6)_2$ (**5**-$(PF_6)_2$): Anal. Calcd for $C_{32}H_{40}Cu_2F_{12}N_6OP_2$: C, 40.81; H, 4.28; N, 8.92. Found: C, 40.71; H, 4.19; N, 9.38. UV–vis (CH_3CN): λ_{max} = 370 (ϵ 2040), 619 (130). IR (Nujol) ν (PF) = 840 (s) cm^{-1}. μ_{RT} = 1.01 μ_B/Cu. Λ_m (CH_3CN) = 297 Ω^{-1} cm^2 mol^{-1}.

[16] At −75 °C by addition of NO(g) over a solution of **6**, FT-IR spectra were recorded using an internal-reflection probe incorporated as part of the low-temperature glass reaction vessel; Spectra-Tech Applied Systems, Inc., ReactIR Reaction Analysis System.

[17] (a) A $\{Cu–NO\}^+$ adduct formed from $1Cu^I$ + NO(g) would be expected to be paramagnetic and thus EPR active. The low ν_{NO} and low-energy vis absorption (d–d transition) suggest a $Cu^{II}–NO^-$ description, with a dinuclear formulation accounting for EPR silence through an antiferromagnetic coupling interaction. (b) **7** is unlikely to be a $Cu–N_2O$ species; we observe that N_2O does not react with any of the Cu complexes used in these studies, and $M–N_2O$ species are rare.[1b] See: Vaughan, G. A.; Rupert, P. B.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 5538–5539.

[18] $[\{Cu(TMPA)\}_2O](PF_6)_2 \cdot CH_2Cl_2$ (**8**-$(PF_6)_2 \cdot CH_2Cl_2$): Anal. Calcd for $C_{37}H_{38}Cl_2Cu_2F_{12}N_8OP_2$: C, 40.45; H, 3.49; N, 10.20. Found: C, 40.47; H, 3.43; N, 10.64. UV–vis (C_2H_5CN): λ_{max} = 403 (ϵ 530), 736 (220), 900 (320). IR (Nujol) ν(PF) = 845 (s) cm^{-1}. μ_{RT} = 1.73 μ_B/Cu. Λ_m (CH_3CN) = 259 Ω^{-1} cm^2 mol^{-1}.

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[20] Reaction of NO_2^- with **2** may generate a $[Cu^{II}–(N_2O_3^{2-})–Cu^{II}]$ (e.g., attack on NO^-) or $[(NO^-)–Cu^{II} \cdots Cu^{II}–(NO_2^-)]$ (e.g., attack on Cu^{II}) species.[3b]

New Chiral Ligand for the Asymmetric Conjugate Addition of Organocopper Reagents to Enones

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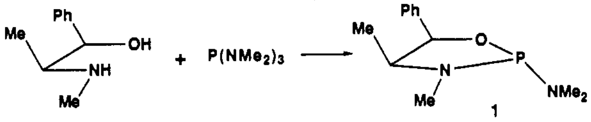
The asymmetric version of the conjugate addition reaction of organocopper reagents to enones is a long-pending problem. In the case of *achiral* enones this reaction was attempted either with chiral heterocuprates[1] or with chiral ligands.[2] Among the ligands of copper, trivalent phosphorus derivatives are the best ones,[3] and we thought that chirality on the phosphorus atom itself would induce asymmetry during the conjugate addition. We present herein our results with the chiral phosphorus derivative **1**, which demonstrate, for the first time, the effectiveness of this class of ligands in the conjugate addition of organocopper reagents. This compound[4] is easily and quantitatively prepared from (−)-ephedrine and HMPT (eq 1) and is configurationally homogeneous at the phosphorus stereogenic center. In the same manner were also prepared the phosphorus derivatives **2**, **3**, **4**,[5] **5**,[6] and **6**[7] (Scheme I).



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(1)

Derivatives **1–6** form soluble complexes with a CuX (X = Br, I) salt in Et_2O or THF. Reaction with an organolithium or Grignard reagent gives rise to an organocopper or cuprate derivative, according to the stoichiometry. The transfer of the nBu

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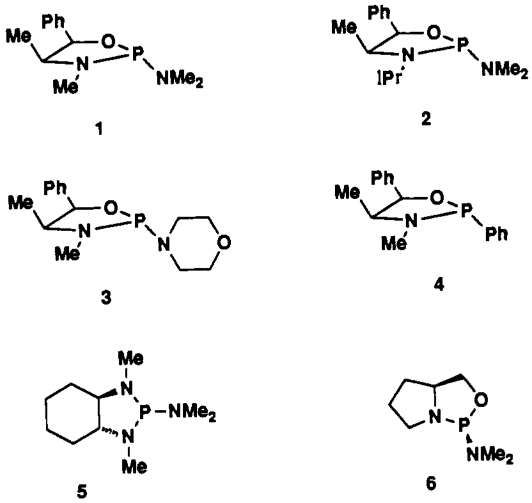
Table I. Reactions with Organocopper Reagents Complexed with Ligands **1**–**6**

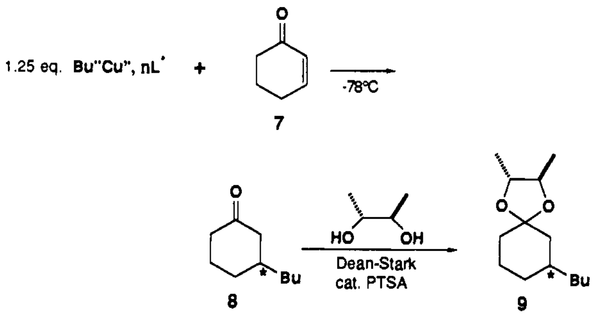
entry	BuM[a]	ligand	copper source and added salts	amount of ligand, equiv	solvent	chem yield[b] (of **9**), %	ee, %
1	BuLi/hexane	**1**	CuI	1	THF	30	22
2	BuLi/hexane	**1**	CuI	2	THF	35	38
3	BuLi/hexane	**1**	CuI	3	THF	43	19
4	BuLi/hexane	**1**	CuI	2	Et_2O	43	22
5	BuLi/hexane	**1**	CuI + TMSCl	2	THF	15	*rac*
6	BuLi/hexane	**1**	CuI + 4LiBr	2	THF	56	*65*
7	BuLi/hexane	**1**	CuI + 4LiI	2	THF	45	44
8	BuLi/hexane	**1**	$CuBr{\cdot}Me_2S$ + 4LiBr	2	THF	45	40
9	$BuLi{\cdot}LiBr/Et_2O$[c]	**1**	CuI + 3LiBr[d]	2	THF	62	*62*
10	$BuMgBr/Et_2O$	**1**	CuI + 4LiBr	2	THF	28	19
11	0.5 equiv BuLi/hexane	**1**	CuI + 4LiBr	2	THF	27	75
12	2 equiv BuLi/hexane	**1**	CuI + 4LiBr	2	THF	>90	0–75
13	BuLi/hexane	**2**	CuI + 4LiBr	2	THF	61	*76*
14	BuLi/hexane	**3**	CuI + 4LiBr	2	THF	10	62
15	BuLi/hexane	**4**	CuI + 4LiBr	2	THF	12	14
16	BuLi/hexane	**5**	CuI + 4LiBr	2	THF	55	*rac*
17	BuLi/hexane	**6**	CuI + 4LiBr	2	THF	62	23

[a] Commercial 1.6 M solution in hexane, except when otherwise noted. [b] Yield of isolated pure ketal **9**. [c] Prepared in Et_2O from BuBr and Li metal. [d] The fourth equivalent of LiBr is brought by the ethereal organolithium solution.

Scheme I



group was systematically studied under various conditions, and this reagent was reacted with 2-cyclohexenone **7** as the model enone. The crude conjugate adduct 3-butylcyclohexanone **8** was then transformed into the diastereomeric ketals **9** by reaction with optically pure (*R*,*R*)-2,3-butanediol[8] in order to determine the chemical yield, the absolute configuration,[1a] and the degree of optical induction (eq 2).



(2)

These reactions were run until no starting material was left. Generally, the cuprate reagents were much more reactive than the copper reagents, the reaction being completed in a few minutes at −78 °C. In all these experiments the adduct **8** has the *R* configuration whereas with the ligand derived from (+)-ephedrine, *ent*-**1**, the *S* adduct is obtained with the same ee. The rationalization of these results, as far as the ee are concerned, is quite difficult, and many of the results are quite puzzling. Nevertheless, there are some trends that seem to be quite general.

Ligand **1** was used as the standard ligand for the optimization studies. From the first three entries in Table I, it is clear that the best ratio of chiral ligand to copper reagent is 2. It is also clear that THF is a superior solvent to Et_2O (entries 2 and 4). The addition of trimethylsilyl chloride (TMSCl)[9] does not have any beneficial effect (entries 2 and 5) either on the chemical yield or on the ee. However, the addition of lithium salts has a strongly beneficial effect on the enantiomeric excess. The best value is 4 equiv. Such a lithium salt effect was not reported in the asymmetric conjugate addition of organocopper reagents. The nature of this lithium salt also seems important, since LiI gave a lower ee than LiBr (entries 6 and 7). The same is true for the Cu(I) salt,[10] where, in contrast, CuI is better than $CuBr{\cdot}Me_2S$ (entries 6 and 8). Excess copper salt has a beneficial effect on the ee, but the low chemical yield is notable (entries 6 and 11). Provided the proper salts are present, the origin of the BuLi does not influence the outcome of the reaction: the yield and the ee are comparable whether a commercial 1.6 M solution in hexane or homemade $BuLi{\cdot}LiBr$ in Et_2O is used (entries 6 and 9); aged bottles also gave the same result.[11] Finally, it should be noted that the organocopper reagent prepared from a Grignard reagent is not efficient in both respects (entries 6 and 10).

Dibutylcuprate reagents were extensively examined. In all instances they gave a quantitative yield of conjugate adduct **8**. However, the ee was highly variable according to the copper source.[10] One crop (from Prolabo) gave excellent results (ee 75%), and another one, from the same company, gave a racemic material! Most other sources of CuI (Aldrich, Fluka, Janssen) gave moderate ee's (30–50%). Highly purified CuI[12] also gave a racemic material. The reason for this variability has yet to be found.

Several other phosphorus ligands were also examined (see Scheme I) under the optimum conditions found for ligand **1** (entry 6: CuI + 4LiBr). Ligand **2** was designed to see the influence of the steric effect on the nitrogen atom. The result was a clear improvement of the ee (entry 13). In ligand **3** the exocyclic NMe_2 was replaced by the morpholino group where an extra chelation by the oxygen is possible. The ee did not change significantly, but the chemical yield was very low (entry 14). A disappointing result was also obtained with ligand **4**, where a P–C bond replaces the exocyclic P–N bond (entry 15). Ligand **5** was prepared with a diamine having a C_2 axis of symmetry; the racemic adduct **8**

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was obtained. Ligand **6**, derived from (–)-prolinol, also gives a very low ee (entry 17).

The results of these model studies[13] indicate that the concept of a chiral phosphorus ligand for organocopper reagents is, indeed, a workable hypothesis. Relevant are the following facts: (a) the addition of extra lithium salts is necessary; (b) 2 equiv of ligand is needed. We are presently extending these results to transferable groups other than nBu and other enones. Since it is easily possible to modify the chiral auxiliary on phosphorus, it seems that there is plenty of room for further improvement in this new class of chiral ligands to copper. Work is in progress toward this end.

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(13) Typical procedure: To a suspension of CuI (476 mg; 2.5 mmol) in THF (40 mL) is added ligand **1** (3.4 mL of a 1.5 N solution in toluene; 5.1 mmol) at –30 °C. The temperature is allowed to rise, and solubilization is usually observed around 10 °C. After stirring for 15 min, the solution is cooled to –40 °C and nBuLi (1.45 mL of a 1.6 M solution in hexane; 2.3 mmol) is added. The solution, which turns yellow, is warmed for 15 min at –5 °C and then cooled again to 78 °C, and 2-cyclohexenone **7** (200 μL; 2 mmol) in THF (5 mL) is introduced. The mixture is then slowly warmed to –30 °C (in 1 h) and stirred until the disappearance of **7**. Hydrolysis was carried out with 15 mL of 5 N HCl, and stirring is continued in the open air for 1 h in order to hydrolyze the ligand completely. The aqueous phase is extracted with two 100-mL portions of ether, and the combined organic phases were then washed twice with NH_4OH in order to remove the copper salts. The solvents were removed in vacuo, and the crude product was treated with (*R*,*R*)-2,3-butanediol in a Dean–Stark trap.[8] The final ketal **9** was purified by flash column chromatography and then by Kugelrohr distillation.

On the Mechanism of Spin Coupling in Metallocenium Charge-Transfer Salts: Ferromagnetism in Decamethylchromocenium Tetracyanoquinodimethanide

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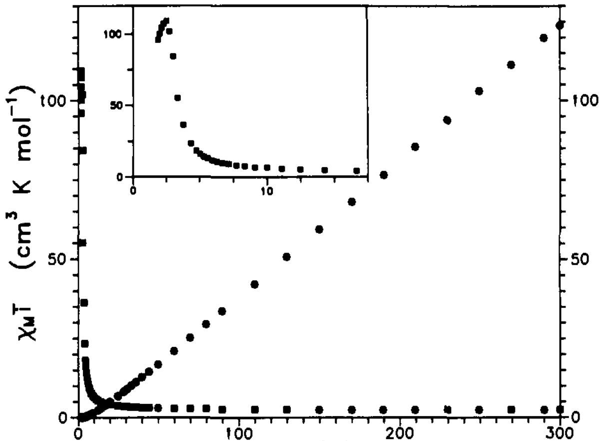

Figure 1. Temperature dependence of $\chi_m T$ (squares) and χ_m^{-1} (circles) for polycrystalline **3** recorded at 250 G. Inset: expansion of the 1.9–15 K region of the $\chi_m T$ plot.

The challenge of creating molecular-based ferro- or ferrimagnets has been addressed in several ways.[1-7] Among them, the search for ferromagnetic donor–acceptor (D^+A^-) charge-transfer (CT) salts[3-6] has been dominated by a "prescription"[3] inspired by McConnell's[2a] recognition that ferromagnetic spin coupling within an interacting D^+A^- pair might arise through configuration mixing with a virtual CT state, provided that D^+ or A^- possesses an orbitally degenerate ground state. The $[Fe(C_5(CH_3)_5)_2]^+$ ($S = {}^1/_2$, ${}^2E_{2g}$) and $[Mn(C_5(CH_3)_5)_2]^+$ ($S = 1$, ${}^3E_{2g}$) cations have such a ground state.[8] Their mixed-stack, ...$D^+A^-D^+A^-$..., salts with orbitally nondegenerate paramagnetic counterions thus fulfill the requirements of the CT configuration mixing mechanism[3] and, indeed, typically display ferromagnetic behavior,[3a,4] with $[Fe(C_5(CH_3)_5)_2][TCNE]$[9] (**1**) and $[Mn(C_5(CH_3)_5)_2][TCNQ]$[4a] (**2**) being bulk ferromagnets.

However, the behavior of the $[M(C_5(CH_3)_5]^+$ CT salts where M = Fe or Mn does *not* validate this mechanism, for its predictions in these two cases coincide with those of alternate mechanisms for spin coupling, namely, Heisenberg exchange between electrons in orthogonal orbitals[10,11] and spin-polarization-based exchange.[2b,12] In contrast, CT configuration mixing would lead to antiferromagnetic D^+–A^- coupling for the orbitally nondegenerate $[Cr(C_5(CH_3)_5)_2]^+$ ($S = {}^3/_2$, ${}^4A_{1g}$)[8] cation, whereas the alternate mechanisms would lead to ferromagnetic D^+–A^- coupling. Thus, CT salts with M = Cr serve as a clear test of the spin-coupling mechanism in this class of materials. We report here that the 1:1 CT salt $[Cr(C_5(CH_3)_5)_2][TCNQ]$ (**3**) not only displays fer-

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