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Some studies involving the use of chiral amine oxides for the enantioselective preparation of (propargyl alcohol)$Co_2(CO)_5(PR_3)$ complexes

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Abstract

The enantioselective preparation of (propargyl alcohol) dicobalt pentacarbonylphosphine complexes (**2**) via kinetic resolution with an optically active amine oxide was examined. Variations in temperature, solvent, phosphine, amine oxide, and substrate were studied. Diastereoselectivity showed marked improvement over thermal methods, while enantioselectivity was modest. The typical e.e. for product **2a** was 20% at 30–40% conversion when the reaction was carried out at −58°C in a 1:1 mixture of tetrahydrofuran/dichloromethane with brucine *N*-oxide as the promoter.

Keywords: Chiral amine oxide; Enantioselective preparation; (Propargyl alcohol)$Co_2(CO)_5(PR_3)$ complexes

1. Introduction

The distinctive reactivity and structure of dicobalt propargyl alcohol complexes (**1** and **2**, Eq. (1)) and the derived cations **3** has led to considerable exploitation of their synthetic utility by our research group and others [1,2]. It was anticipated that an asymmetric cobalt cluster (as in **2**) should provide facial selectivity in the reactions of cobalt-stabilized propargyl cations or radicals, thereby leading to enantiomerically-enriched complexes and, ultimately, optically active organic products [3]. Given stereocenters at both C1 [4] and at the cobalt cluster, four stereoisomers (two diastereomers, each as a pair of enantiomers) can be formed in the ligand substitution reaction, as shown in eq. 1 (the configuration of only one of the stereogenic cluster carbons is shown since the second carbon's configuration is dependent on the first [5–7]).

The ongoing need for stereoselective methods for the preparation of optically pure organic molecules has motivated our continuing pursuit of efficient enantioselective routes to chiral cobalt complexes of type **2**. Numerous powerful methodologies in organic synthesis take advantage of asymmetric induction by organometallic compounds, but classical methods for the preparation of homochiral organometallic complexes are typically lengthy and often require a tedious resolution step. Generation of a chiral metal center frequently requires ligand substitution, most often replacement of CO by a phosphine or similar ligand. The standard methodology for ligand substitution, e.g. thermal or photochemical labilization of CO, frequently requires stringent reaction conditions, potentially causing epimerization of metal stereocenters. In contrast, the amine oxide-induced replacement of carbonyl ligands is a remarkably mild transformation [8] which has found use in the acceleration of the Pauson–Khand reaction [9–11]. Kerr et al. have recently demonstrated that the use of enantiomerically enriched chiral amine oxides with prochiral (alkyne)$Co_2(CO)_6$ complexes in this reaction results in low to moderate asymmetric induction [12]. These researchers have also reported an elegant achiral amine oxide-promoted preparation of optically pure dicobalt (alkyne) pentacarbonylphosphine complexes using a chiral phosphine ligand [13,14]; Brunner and coworkers had prepared such complexes earlier by direct thermal substitution [13,14].

In order to prepare **2** in optically pure form, stereocontrol at both C1 and the cobalt cluster must be considered. Our previous work [5–7] demonstrated that control at the cluster is possible with moderate to high diastereoselectivity in thermal reactions of **1** with L=PPh_3 and that the

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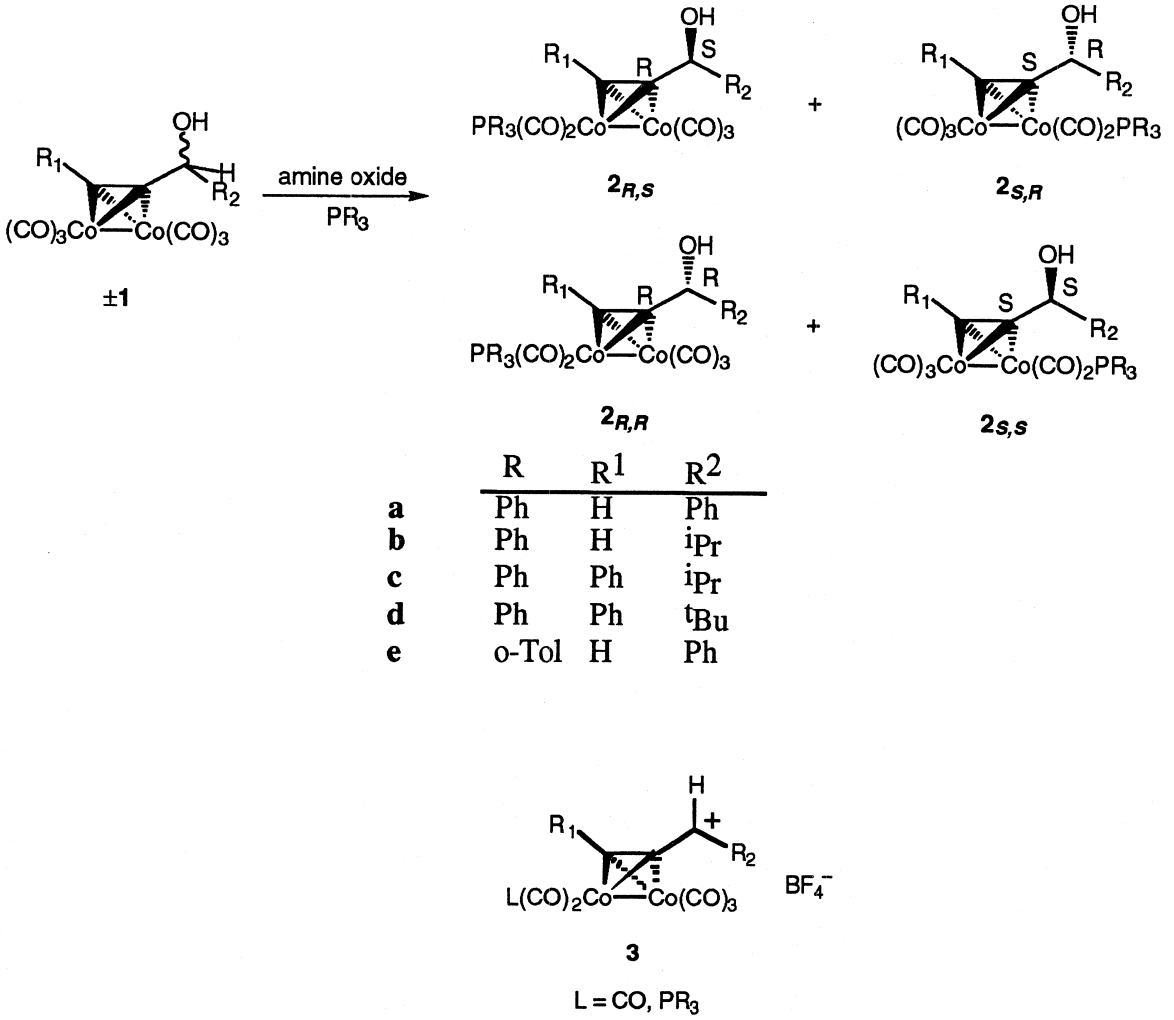
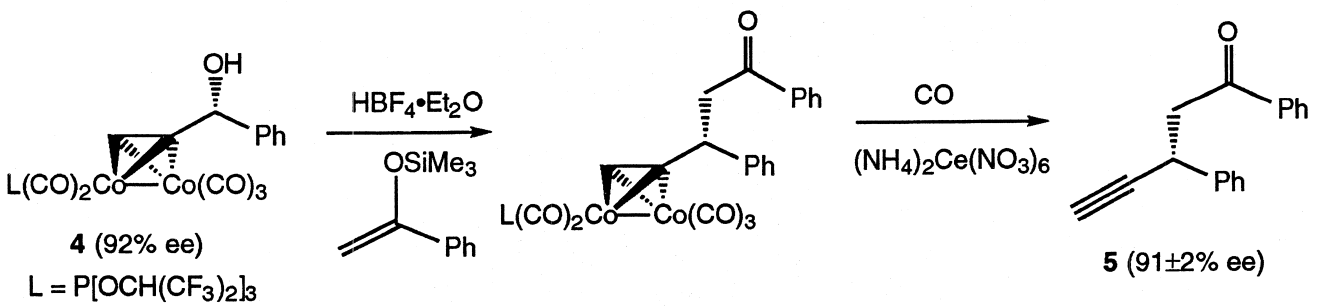


	R	R^1	R^2
a	Ph	H	Ph
b	Ph	H	^{i}Pr
c	Ph	Ph	^{i}Pr
d	Ph	Ph	^{t}Bu
e	o-Tol	H	Ph

(1)

cluster is configurationally stable, an important consideration in the development of enantioselective variants of subsequent reactions. Furthermore, use of optically active propargyl alcohol complex **4** as shown in Scheme 1 [3] resulted in the formation of product **5** with the same e.e. as starting material **4**, providing evidence for the stability of the cations **3** to cluster epimerization, and showing promise for enantioselective propargylation.

Stimulated by these findings and in communication with the Kerr group we sought to evaluate the potential of optically pure amine oxides for the enantioselective and diastereoselective preparation of phosphine-substituted cobalt propargyl alcohol complexes as shown in Eq. (1). This novel approach to optically active cobalt propargyl alcohol complexes has as its key feature the kinetic resolution of racemic **1** by reaction with a homochiral amine oxide in the presence of an achiral phosphine. The basic premise of the resolution is straightforward. Let k_r be



Scheme 1. Enantioselective propargylation by a chiral (propargyl alcohol)$Co_2(CO)_5(PR_3)$ complex.

the rate constant for conversion of the *R* enantiomer of **1** into product, and k_s the rate constant for conversion of the *S* enantiomer. If $k_r \gg k_s$, stopping the reaction prior to 100% conversion allows recovery of starting material enriched in the *S* isomer and, ideally, optically pure product. A similar approach to the preparation of optically active organometallic complexes was first demonstrated by von Phillipsborn and co-workers [15] in the preparation of optically active enone–iron carbonyl complexes. The present system is exceptional in that a new stereocenter at the metal cluster is created in the course of the kinetic resolution. Few other kinetic resolutions of chiral organometallic complexes can be found in the literature, and these typically involve reaction of the resolving reagent at the organic ligand rather than at the metal center(s) [16,17].

2. Experimental

All reactions were carried out under a positive pressure of dry high-purity nitrogen. Diethyl ether, dioxane and tetrahydrofuran were dried and distilled from sodium/benzophenone ketyl. Dichloromethane and acetonitrile were dried and distilled from calcium hydride under an atmosphere of nitrogen. Methanol was dried and distilled from 4Å molecular sieves. The (propargyl alcohol)$Co_2(CO)_6$ (**1a–d**) and (propargyl alcohol)$Co_2(CO)_5(PPh_3)$ (**2a–d**) complexes were prepared as reported previously [5]. The amine oxides **6–9** were prepared by oxidation of the corresponding amine with hydrogen peroxide (Brucine N-oxide, W.J. Kerr, personel communication; [31–33]). Analysis of e.e. was carried out using an ISCO HPLC system equipped with a Chiralpak AD column, eluted with a 2:98 mixture of isopropanol in hexanes, and detected at λ_{254} nm.

2.1. General procedure for kinetic resolution of phosphine substituted complexes (2)

To a stirred and cooled solution (−58±4°C) of racemic hexacarbonyl cobalt complex (**1**, 1.0 mmol)) under nitrogen in a 1:1 mixture of tetrahydrofuran/dichloromethane was added slowly a slurry of amine oxide (0.5 mmol) and triphenylphosphine (1.0 mmol), premixed in the same solvent mixture. The reaction progress, over a period of up to several days, was monitored by removing aliquots of the reaction mixture, flashing them through a small pad of silica gel to remove the amine/amine oxide, and injecting the sample on the HPLC.

Mono-phosphinated products were characterized by comparison to known samples. New complexes **1d** and **2d** were characterized by ^{1}H NMR; complex **2e** was not characterized further because of its rapid decomposition. **1d** (^{1}H NMR, C_6D_6) 1.00 (s, 9H), 1.78 (d, 1H, J=4.5 Hz), 4.62 (d, 1H, J=4.8 Hz), 7.04 (m, 1 H), 7.11 (app t, 2H), 7.58 (d, 2H, J=7.5 Hz); **2d** (^{1}H NMR, C_6D_6) 1.02 (s, 9H), 1.77 (d, J=4.5 Hz, 1 H), 3.60 (m, 1H), 7.00–7.40 (m, 20 H).

3. Results and discussion

The effects of variations in temperature, solvent, substrate, phosphine and amine oxide on the diastereoselectivity, enantioselectivity and rate of the reaction were investigated. Additionally, variations in both stoichiometry and procedure were examined in an attempt to optimize the enantioselectivity of the reaction. The standard reaction protocol consisted of adding a slurry containing the phosphine and the amine oxide to a stirred, cooled solution of racemic hexacarbonyl cobalt complex (**1**). The reaction progress (specifically, the change in e.e. of both **1** and **2** with time) was monitored by analyzing aliquots from the reaction mixture by HPLC using a chiral column. The products were identified by isolation and comparison with authentic (racemic) samples. Most experiments were conducted on the amine oxide-promoted reaction of **1a** with PPh_3. HPLC analysis allowed determination of the enantiomeric composition of both the unreacted alcohol complex **1a** and the major diastereomer of product **2a**; the minor diastereomer of **2a**, however, could not be resolved. The major diastereomer of **2a** produced in the reaction was found to be the *R,S/S,R* isomer, which also dominates in the purely thermal reaction [5].

3.1. Temperature effects.

Several initial experiments were carried out to determine the effect of temperature on diastereoselectivity in reactions of **1a** with PPh_3 and to find the optimum temperature at which to carry out subsequent reactions. As expected, diastereoselectivity increased as the temperature decreased (from 38% d.e. at −15°C to 52% d.e. at −30°C, 76% d.e. at −60°C, and 78% d.e. at −95°C). Because there appeared to be little improvement in diastereoselectivity below −60°C, a standard temperature of −58±4°C was used for all subsequent reactions. As would be expected for a typical kinetic resolution, the e.e. of the unreacted starting material slowly increased from its initial value of zero to as high as 26% e.e. at moderately high conversion (63%). Fig. 1 shows the change in e.e. of the unreacted starting material as a function of percent conversion, as well as the change in e.e. and d.e. of the major diasteromer of **2a** for a representative reaction. Interestingly, the e.e. of the product did not decrease steadily with time, as would be expected in the case of a simple kinetic resolution [18,19]. Unfortunately, because we could not assess the e.e. of the minor diastereomer (op cit), it is impossible to account for this curious behavior. This effect could be the result of epimerization of the minor to the major diastereomer.

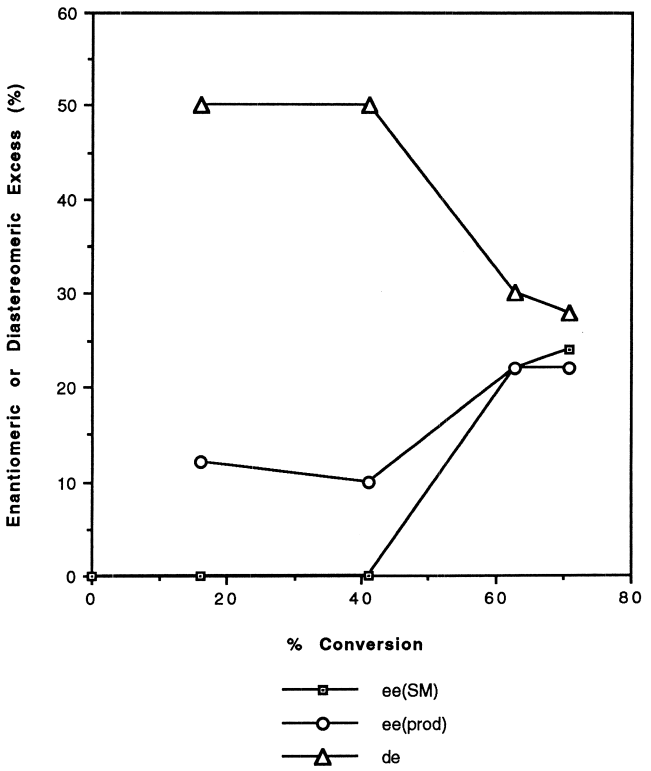


Fig. 1. Stereoselectivity versus conversion for the reaction of **1a** with PPh_3 promoted by brucine *N*-oxide at −58°C in 1:1 THF:CH_2Cl_2. Percentage e.e. of **2a** is that of the major (*RS*, *SR*) diastereomer.

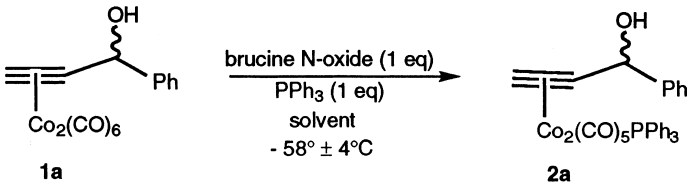
3.2. Solvent effects

The nature of the solvent system had a substantial influence on the rate of the reaction, as has been seen in other amine oxide-promoted substitutions [9–12]. Both protic and aprotic solvents with a range of coordinating ability were tested. Use of acetone/CH_2Cl_2 or acetonitrile/CH_2Cl_2 increased the rate (Table 1, cf. entries 1 versus 2, 1 versus 5), suggesting the involvement of a coordinatively unsaturated intermediate [8–11]. However, no enhancement of stereoselectivity was seen with these solvents. Variations in the ratio of the tetrahydrofuran/dichloromethane co-solvent system similarly had little impact on the selectivity of the reaction (cf. entries 1 and 6, Table 1), and was complicated due to the insolubility of the reagents. Similar solubility difficulties were encountered when using ether or dioxane in place of tetrahydrofuran and lower enantioselectivity also resulted (entries 7 and 8, Table 1). The use of methanol resulted in a greatly diminished reaction rate (no reaction at −55°C) despite a homogenous reaction mixture, possibly the result of decreased nucleophilicity of the amine oxide oxygen due to hydrogen bonding with the solvent (entry 3, Table 1) [21].

3.3. Substrate effects

Based on these findings, the influence of the remaining variables (the nature of the propargyl substrate, the phosphine ligand, and the amine oxide promoter) on stereoselectivity was tested under the standard conditions of −58±4°C and in a 1:1 ratio of THF:dichloromethane. Only modest enantioselectivity was observed with complex **1a**, with a typical maximum enantioselectivity for the phosphinated product **2a** (major diastereomer) of about 20% e.e. at approximately 30–40% conversion when brucine *N*-oxide was used as the promoter. As a result, we briefly turned our attention to complexes **1b–d** which bore

Table 1
Effect of solvent on brucine oxide-promoted substitutions



1a **2a**

Entry	Solvent	Time (h)	Conv. (%)	d.e. (%)[a] **2a**	e.e. (%)[b] **1**	e.e. (%) **2a**[c]
1	1:1 THF:CH_2Cl_2	64	33	58	10	20
2	1:1 acetone:CH_2Cl_2	24	51	40	4	0
3	1:1 CH_3OH:CH_2Cl_2	18.5	0	–	–	–
		20[d]	54	54	4	0
4	1:1 CH_3CN:CH_2Cl_2	1.5	19	56	–	16
5	1:9 CH_3CN:CH_2Cl_2	24	22	62	4	0
6	1:19 THF:CH_2Cl_2	48	24	–	–	14
7	1:3 dioxane:CH_2Cl_2	43.5	44	52	6	4
8	1:4 ether:CH_2Cl_2	48	28	58	4	4

[a] Percentage major isomer–percentage minor isomer.
[b] Percentage major enantiomer–percentage minor enantiomer.
[c] Percentage e.e. of major diastereomer.
[d] After initial time at −58°C, reaction was warmed to room temperature.

isopropyl or *tert*-butyl groups. We anticipated that the phosphine substitution could be carried out diastereospecifically due to the increased steric demands of the propargyl R_2 group [5], allowing us to focus on enantioselectivity. Unfortunately, brucine *N*-oxide-promoted triphenylphosphine substitution of complex **1b** stubbornly yielded a mixture of diastereomers (26% d.e. after 48 h at −55°C). Complex **1c** underwent the brucine *N*-oxide-promoted substitution reaction diastereospecifically, but the monosubstituted product was contaminated with a small amount of the bis-phosphinated complex. This contaminant was inseparable by chromatography, thus rendering the HPLC analysis of enantioselectivity unreliable. Further investigations with both **1b** and **c** were therefore abandoned. Triphenylphosphine substitution of complex **1d** proceeded smoothly to yield a single diastereomeric product, but the complex failed to resolve on the chiral HPLC column. The decomplexed alcohol, however, did resolve, hence enantioselectivity was monitored by removing an aliquot from the reaction mixture, separating the starting material from the product by flash silica gel chromatography, decomplexing the alcohol from product **2d** with ceric ammonium nitrate, and injecting the crude alcohol on the HPLC. A promising e.e. of 40% was observed after 72 h at −55°C, but the e.e. of the decomplexed alcohol varied erratically with time, possibly due to racemization or incomplete separation of the starting complex from the product during workup.

3.4. Phosphine effects

The encouraging results seen with complex **1d** suggested that the selectivity of the reaction could be improved by increasing the steric demands of the other species presumably involved in the transition states (e.g. the amine oxide and the phosphine). Accordingly, tri(*o*-tolyl) phosphine was employed in place of triphenylphosphine. Unfortunately, the resulting monophosphinated complex **2e** was found to decompose readily under the reaction conditions. This finding, in conjunction with the expense of tri(*o*-tolyl) phosphine and its relatively lacklustre selectivity (the system peaked at 12% e.e. for product **2e**), resulted in its rejection as a viable alternative.

3.5. Amine oxide effects

Brucine *N*-oxide (**6**), sparteine *N*-oxide (**7**), quinine *N*-oxide (**8**), and two proline derivatives (**9a** and **b**), all prepared by oxidation of the corresponding amines with hydrogen peroxide, were studied to determine their effect on the stereoselectivity of the reaction.

Brucine *N*-oxide (BNO) was the most effective amine oxide in terms of ease of preparation, convenience (solubility), and consistency of results: the e.e. for the preparation of complex **2a** was typically 20% when BNO was used. Furthermore, brucine *N*-oxide consistently gave the highest e.e. Use of sparteine *N*-oxide (in place of BNO) ultimately resulted in a large decrease in the diastereoselectivity (8% d.e. at 97.5 h and 47% conversion), with the amount of minor diastereomer steadily increasing with time [20]. Quinine *N*-oxide initially showed a similar negative impact on the diastereoselectivity (18% d.e. after 30 h and 5% conversion), but in this case, the diastereoselectivity *increased* with increasing reaction time (eventually reaching 64% d.e. at 52% conversion; entry 3, Table 2). The choice of amine oxide also profoundly affected the rate of the reaction. Reaction of **1a** with the proline-derived amine oxides **9a–b** was dramatically slower as was the reaction with quinine *N*-oxide (entries 4 and 5, Table 2). This phenomenon was attributed in part to the reduced solubility of the amine oxide in the reaction medium, but the reduced nucleophilicity of the amine oxide oxygen (due to intramolecular hydrogen bonding) may play a role as well. Even in a homogenous aprotic reaction medium, the reaction rate was excruciatingly slow.

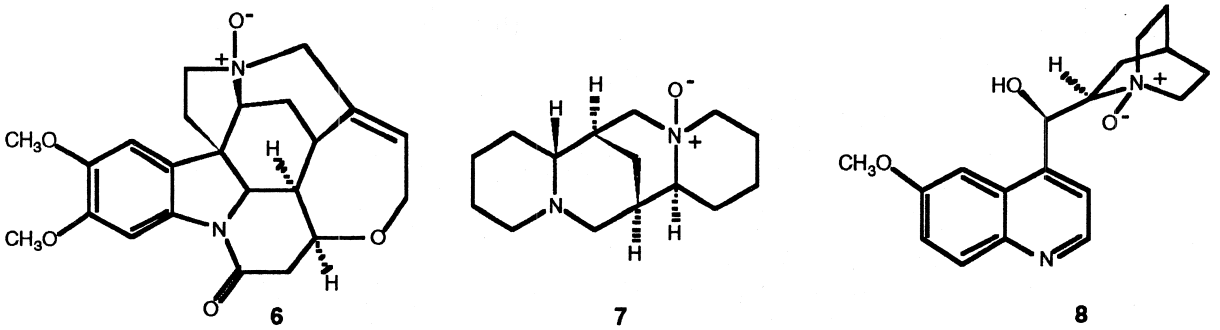
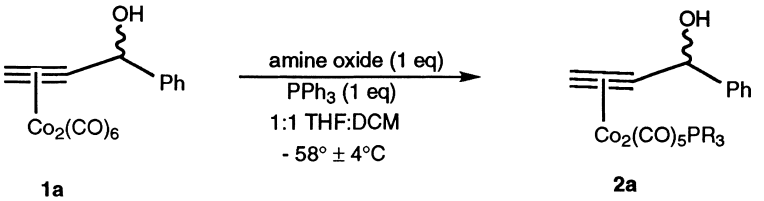


Table 2
Effect of amine oxide on substitutions



1a **2a**

Entry	Amine Oxide	% conv.	d.e. (%) **2a**[a]	e.e. (%) of **2a**[b]
1	6	33	66	20
2	7	43	22	4
3	8	52	64	2
4	9b	11	72	0

[a] Percentage major isomer–percentage minor isomer.
[b] Of major (*RS*/*SR*) diastereomer.

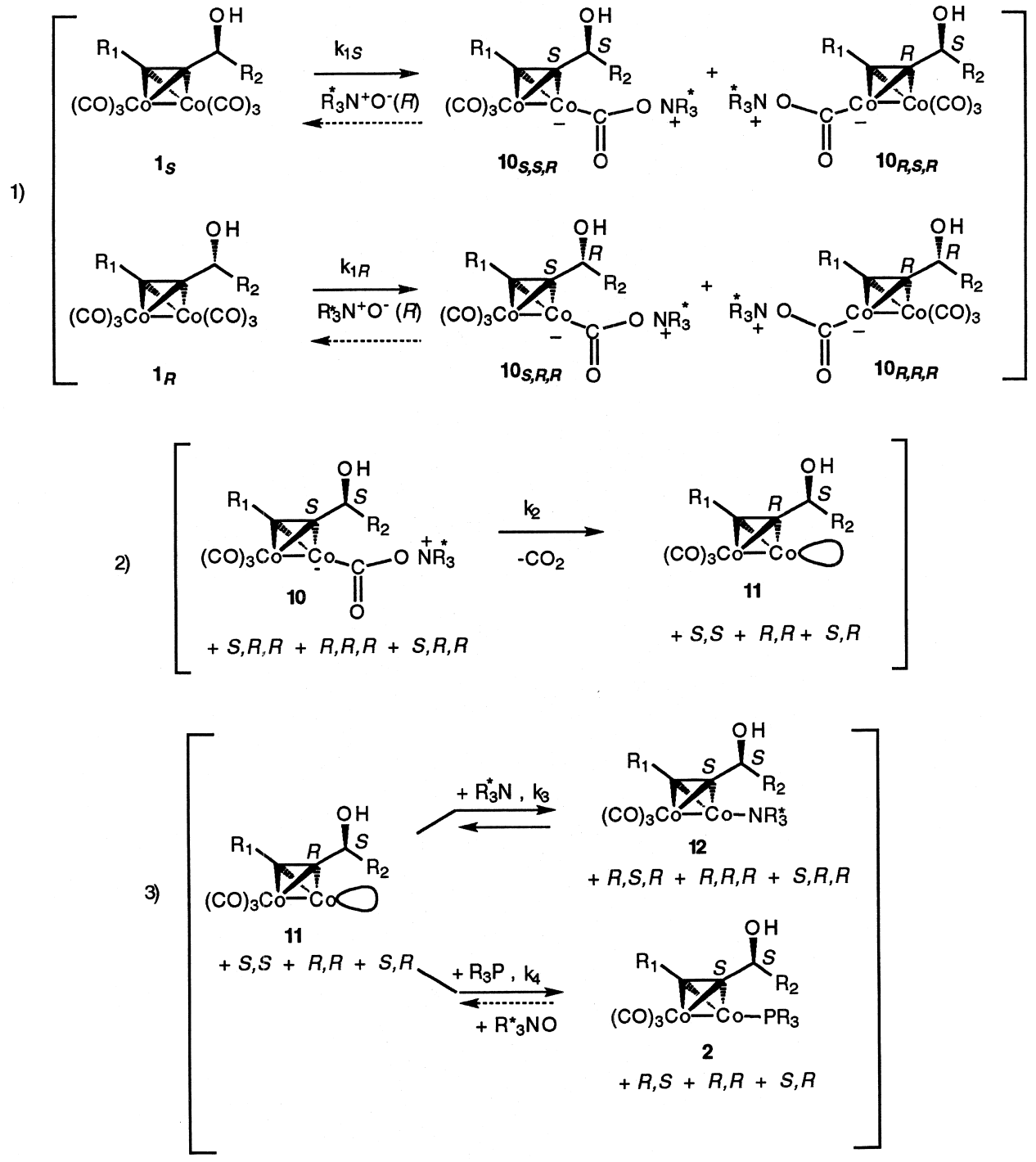
3.6. Other effects

Given the modest enantioselectivity described above, we turned our attention to other modifications of the procedure. Interestingly, the enantioselectivity was considerably improved by the addition of one-half equivalent of brucine (in addition to the brucine *N*-oxide). In this trial, the e.e. of **2a** was increased to 32% at 20% conversion. The presence and amount of the additional amine was apparently critical, as addition of two equivalents of brucine returned the e.e. to typical values (18% at 50% conversion with a d.e. of 66%). Addition of four equivalents of brucine *N*-oxide yielded similarly lackluster results (12% e.e. at 20% conversion).

While the enantioselectivities observed in these reactions were modest, amine oxide promotion did provide several advantages over the thermal preparation. The formation of the bis-phosphinated complex $(PPh_3)_2(CO)_4Co_2(HC{\equiv}CCHOHPh)$ was completely suppressed, for example (as also observed by Kerr et al. [13,14]). Furthermore, a dramatic increase in rate and a significant increase in diastereoselectivity was observed. Earlier studies demonstrated that, under thermal conditions (50°C), triphenylphosphine substitution on complex **1a** takes place with 60% d.e. [5–7]; both the thermal and the amine oxide-promoted conditions yielding the same major diastereomer ($\mathbf{2a}_{SR/RS}$). The observed diastereomeric excess for the amine oxide-promoted substitution reactions of this complex varied with the extent of reaction (Fig. 1), typically reaching a maximum in the first several hours of the reaction, then slowly leveling off. The maximum diastereomeric excess for **2a** was 74%, achieved after a reaction time of 4 h (21% conversion) in a solvent mixture of 25:75 diethyl ether/dichloromethane at −62°C. The variation of percentage d.e. with time suggests that even at low temperatures equilibration of the minor diastereomer to the major diastereomer may be taking place. Since previous studies have demonstrated that this equilibration takes place only very slowly at 20°C in the absence of added ligands [5–7], the amine oxide and/or the derived amine apparently facilitates the epimerization process.

Although the levels of enantioselection observed in these reactions are not practically useful, this study does provide the first examples of kinetic resolution of racemic (alkyne)$Co_2(CO)_5L$ complexes. The origin of the enantioselectivity in this system, however, appears to be complex, as indicated by the unexpected increase in the e.e. of the product **2** with increasing conversion (Fig. 1) as well as some of the effects of solvent change and the addition of brucine to the reactions. Clearly this system does not adhere to the description of a simple kinetic resolution. Kagan and others [18,19] have demonstrated that, in systems where an asymmetric center is created in the resolving process (as is the case here), the e.e. of the diastereomeric products is interdependent upon a number of factors, including the e.e. and fractional amount of each chiral species, as well as the extent of conversion. The complex interplay of these effects can cause dramatic deviations from the typical e.e. versus conversion behavior.

In the present system, the enantioselectivity must result from discrimination between diastereomeric transition states (or intermediates) involving the homochiral amine oxide and a complexed propargyl alcohol species. A number of such species may be playing a role in determining enantioselectivity. The proposed mechanism for amine oxide-promoted substitutions begins with initial nucleophilic attack at a coordinated carbonyl ligand by the amine oxide (**10**, Scheme 2), [8,21–26]. It is generally accepted that this initial step is followed by loss of CO_2 to generate a coordinatively unsaturated intermediate (**11**) [8–11]; however, experimental evidence for this intermediate and subsequent steps is limited. Intermediate **11** may be stabilized by coordination of the amine generated in situ from the decarboxylation (giving **12**) [22–27] but is likely that the phosphinated products **2** derive from



[a]Some CO ligands have been omitted for clarity; [b]configuration of R^*_3NO assumed to be *R*

Scheme 2. Proposed kinetic resolution mechanism for ligand substitution of (propargyl alcohol)$Co_2(CO)_6$ complexes.

phosphine trapping of **11**, given the dissociative mechanism implicated for thermal ligand substitution of (alkyne)$Co_2(CO)_6$ complexes [28,29].

Formation of the chiral species **10** in step one (Scheme 2) could be the primary stereodifferentiating step, with subsequent steps having no further impact on the e.e. of the product. Evidence that this is not the sole source of stereodifferentiation, however, is provided by: (1) the observed percentage e.e. of **2** versus conversion behavior and (2) the fact that when **1a** was treated with one equivalent of BNO but no added phosphine over a period of 217 h at −62°C, unreacted **1a** remained racemic (as monitored by HPLC). It is possible that the breakdown of intermediate **10** also could be enantioselective: i.e. if $k_{2R} \neq$

k_{2S} and, if step 2 is rate-limiting (or step 1 is reversible), then it could impact the overall stereoselectivity. Moreover, our finding that addition of one-half equivalent of brucine to the reaction mixture improves enantioselectivity suggests that step 3 (formation of the amine-coordinated complex **12**) also plays a role in the developing enantioselectivity. Thus, stereoselectivity could arise at a number of steps, and each step could, conceivably, either reinforce the selectivity seen in a previous step or counteract it. It is also important to note that, if the enantioselectivity is established en route to the formation of **11**, epimerization of the cobalt cluster at this stage (e.g. by formation of symmetrical bridging carbonyl intermediates) would obviously compromise any enantioselectivity achieved up to this point.

The modest enantioselectivities seen in this reaction, the critical dependence on reaction conditions to maintain this fragile enantioselectivity, and the unusual trends in selectivity seen over the course of the reaction all indicate that this is a complex system. In conclusion, we have found that the use of chiral amine oxides – in particular, brucine *N*-oxide – results in a greatly accelerated carbonyl substitution reaction with an increase in diastereoselectivity over thermal processes, and with significant but modest enantioselectivity.

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References

[1] K.M. Nicholas, Acc. Chem. Res. 20 (1987) 207.
[2] A.J.M. Caffyn, K.M. Nicholas, in: L.S. Hegedus (Ed.), Comprehensive Organometallic Chemistry II, Vol. 12, Elsevier, Oxford, 1995, Ch. 7.1.
[3] A.J.M. Caffyn, K.M. Nicholas, J. Am. Chem. Soc. 115 (1993) 6438.
[4] Numbering C1 as the hydroxyl-bearing carbon.
[5] D.H. Bradley, M.A. Khan, K.M. Nicholas, Organometallics 8 (1989) 554.
[6] D.H. Bradley, M.A. Khan, K.M. Nicholas, Organometallics 11 (1992) 2598.
[7] D.H. Bradley, Ph.D. dissertation, University of Oklahoma, 1992.
[8] M.O. Albers, N.J. Coville, Coord. Chem. Rev. 53 (1984) 227.
[9] S. Shambayati, W.E. Crowe, S.L. Schreiber, Tetrahedron Lett. 31 (1990) 5289.
[10] N. Jeong, Y.K. Chung, B.Y. Lee, H.L. Lee, S.-E. Yoo, Synlett (1991) 204.
[11] M.E. Krafft, I.L. Scott, R.H. Romero, S. Feibelmann, C.E. Van Pelt, J. Am. Chem. Soc. 115 (1993) 7199.
[12] W.J. Kerr, G.G. Kirk, D. Middlemiss, Synlett (1995) 1085.
[13] W.J. Kerr, G.G. Kirk, D. Middlemiss, J. Organomet. Chem. 519 (1996) 93.
[14] H. Brunner, A. Niedernhuber, Tetrahedron: Asymmetry 1 (1990) 711.
[15] B.R. Bender, M. Koller, A. Linden, A. Marcuzzi, W. vonPhillipsborn, Organometallics 11 (1992) 4268.
[16] S. Top, G. Jaouen, C. Baldoli, P. Del Buttero, S. Maiorana, J. Organomet. Chem. 413 (1991) 125.
[17] N.W. Alcock, D.H. Crout, C.M. Henderson, S.E. Thomas, J. Chem. Soc., Chem. Commun. (1988) 746.
[18] H.B. Kagan, J.C. Fiaud, Topics in Stereochemistry 18 (1988) 249, Review.
[19] V.S. Martin, S.S. Woodward, T. Katsuki, Y. Yamada, M. Ikeda, K.B. Sharpless, J. Am. Chem. Soc. 103 (1981) 6237.
[20] The percentage conversion changed very little while the d.e. steadily decreased, suggesting that the presence of either sparteine *N*-oxide or sparteine may have facilitated selective decomposition of the major diastereomer.
[21] J.-K. Shen, Y.-C. Gao, Q.-Z. Shi, A.L. Rheingold, F. Basolo, Inorg. Chem. 30 (1991) 1868.
[22] Y.-C. Gao, Q.-Z. Shi, D.L. Kershner, F. Basolo, Inorg. Chem. 27 (1988) 188.
[23] J.K. Shen, Y.-C. Gao, Q.-Z. Shi, F. Basolo, J. Organomet. Chem. 401 (1991) 295.
[24] J.K. Shen, Y.-C. Gao, Q.-Z. Shi, F. Basolo, Organometallics 8 (1989) 2144.
[25] Y. Shvo, E. Hazum, J. Chem. Soc., Chem. Commun. (1975) 829.
[26] J.H. Eekhof, H. Hogeveen, R.M. Kellogg, J. Chem. Soc., Chem. Commun. (1976) 657.
[27] J. Elzinga, H. Hogeveen, J. Chem. Soc., Chem. Commun. (1977) 705.
[28] R.F. Heck, J. Am. Chem. Soc. 85 (1963) 657.
[29] F. Basolo, A. Wojcicki, J. Am. Chem. Soc. 83 (1961) 520.
[30] Other researchers have similarly searched for such evidence; see ref. [7].
[31] F. Galinovsky, W. Fischer, Monatshefte für Chemie 87 (1959) 763, sparteine *N*-oxide.
[32] H. Diaz-Arauzo, J.M. Cook, J. Nat. Prod 53 (1990) 112, quinine *N*-oxide.
[33] I.A. O'Neil, N.D. Miller, J.V. Barkley, C.M.R. Low, S.B. Kalindjian, Synlett (1995) 617, proline *N*-oxide (9a/b).