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Mild and efficient preparation of alkynepentacarbonyldicobalt complexes containing the chiral (*R*)-(+)-Glyphos ligand

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Abstract

A range of diastereomeric alkynepentacarbonyldicobalt complexes containing the (*R*)-(+)-Glyphos ligand have been prepared in moderate to good yields under standard thermal conditions. Additionally, novel tertiary amine *N*-oxide mediated reactions have been developed which allow the synthesis of the same range of complexes at room temperature with good selectivity in consistently high yields. Optically pure (*R*)-(+)-Glyphos containing complexes have been obtained by preparative HPLC separation of the sets of diastereomeric compounds. Finally, the amine *N*-oxide techniques allow the rapid and clean preparation of alkynepentacarbonyltriphenylphosphinedicobalt complexes in good to high yields at room temperature.

Keywords: Alkyne; Cobalt; Carbonyl; Phosphine; Amine *N*-oxide; Chirality

1. Introduction

Alkyne dicobalt complexes of the type **1** where L = CO are easily prepared and widely used in organic synthesis [1]. Additionally, a variety of complexes where L is a simple phosphine or phosphite ligand (e.g. L = PPh_3, P^nBu_3, PCy_3, and $P(OMe)_3$) are also known [1a,2]. Further consideration of structure **1** reveals that this general class of compound becomes chiral around the C_2Co_2 cluster when $R^1 \neq R^2$ and L ≠ CO. Indeed, diastereomeric complexes of this type, where L = PR_3 or $P(OR)_3$ and the alkyne possesses an enantiomerically pure centre, have been reported [3]. Furthermore, Pauson and coworkers have also shown, in one example, the synthesis of diastereomeric phenylacetylenedicobalt complexes containing a homochiral phosphine ligand [4].

The most common method for the synthesis of phosphorus containing alkynepentacarbonyldicobalt complexes is by ligand substitution of the parent hexacarbonyl species. In the majority of cases reported to date, the replacement of CO by a phosphine or phosphite has been carried out at elevated temperatures (typically around 70°C), or equivalent forcing conditions [3b], over prolonged reaction times [1a,2]. Using these thermal techniques it has also been reported that, at times, it can be difficult to obtain the monosubstituted complexes without contamination by products of higher substitution [5]. Some milder electrochemical or electron-transfer catalysed (using benzophenone ketyl) techniques for such ligand substitutions have been established [6], but good yields are observed with only a very limited number of substrates and, even following extended reactions, poor yields are more usually achieved [3a,6].

During a programme of research targeted towards the formulation of an efficient enantioselective version [7] of the Pauson–Khand reaction [8], we were required to synthesise a range of alkynepentacarbonyldicobalt complexes containing the chiral phosphine ligand (*R*)-(+)-Glyphos **2**. We now wish to report the development of conditions which allow the facile synthesis of these complexes over short reaction times in consistently high

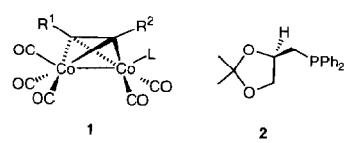

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Fig. 1.

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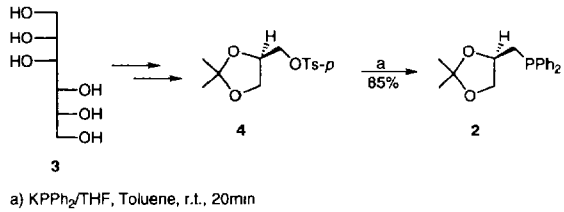


Scheme 1.

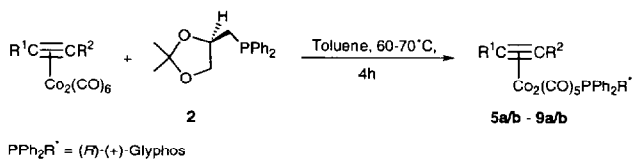
yields under mild conditions. Furthermore, the separation of the resulting diastereoisomers was routinely achieved by preparative HPLC to give optically pure alkynepentacarbonylphosphinedicobalt complexes. The results presented here complement the studies of Anderson et al. presented in the following paper [9], which also reveals techniques for the efficient and convenient formation of phosphorus containing alkyne–dicobalt complexes of this general class.

2. Results and discussion

To initiate our studies the chiral phosphine ligand (*R*)-(+)-Glyphos **2** was synthesised in four steps from D-mannitol **3** in a modification of the known procedures [10]. In particular, the final step involved addition of potassium diphenylphosphide as a THF solution [11] to the tosylate **4**, enabling gram quantities of the chiral ligand **2** to be easily prepared in an improved overall yield of 34% from the readily available D-mannitol starting material (Scheme 1).

Preparation of a range of diastereomeric (*R*)-(+)-Glyphos containing pentacarbonyl complexes was then attempted from the analogous hexacarbonyl species and the chiral ligand **2** under standard, thermal reaction conditions (60–70°C, 4 h) (Scheme 2). As shown in Table 1, formation of three sets of complexes **5a/b–7a/b** was achieved in high yields (78–100%) with the diastereomeric ratios shown. However, in two of these examples (**5** and **7**) a second type of product was also isolated, where two CO ligands had been substituted by two equivalents of the chiral ligand. Furthermore, the final two sets of complexes **8a/b** and **9a/b** were obtained in lower yields under the same general conditions.

Despite being able to obtain the diastereomeric complexes in acceptable yields, the lower conversions (for **8** and **9**) and the requirement for separation of bis-Glyphos compounds constituted reasonable drawbacks to this



Scheme 2.

Table 1
Formation of (*R*)-(+)-Glyphos containing alkynepentacarbonyldicobalt complexes under thermal reaction conditions

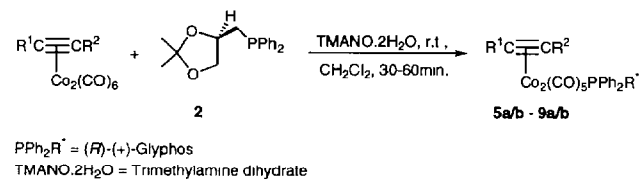
R^1	R^2	Product	Yield (%)	Diastereomeric ratio [a]
Ph	H	**5a/b**	78 [b,c]	60:40
CMe_2OH	H	**6a/b**	100	40:60
CH_2OH	H	**7a/b**	83 [d]	49:51
TMS	H	**8a/b**	68	49:51
TMS	CH_3	**9a/b**	57 [e]	51:49

[a] Calculated by HPLC on a Spherisorb analytical column. [b] Bis-(*R*)-(+)-Glyphos product also isolated in 13% yield. [c] This complex has previously been obtained in similar fashion in slightly lower yields of 55% (Ref. [4]) and 66% (Ref. [12]). [d] Bis-(*R*)-(+)-Glyphos product also isolated in 12% yield. [e] Yield based on recovered starting material.

thermal reaction strategy. Consequently, these limitations prompted us to pursue reaction conditions which would provide an, overall, more efficient process for the synthesis of the desired mono-Glyphos species and alkyne–$Co_2(CO)_5$–phosphine complexes in general.

Over recent years, both in our laboratories [13] and elsewhere [14], tertiary amine *N*-oxides have been used extensively with alkynehexacarbonyldicobalt complexes and alkenes to promote the cyclopentenone forming Pauson–Khand reaction. The remarkable enhancements in reaction efficiency in this annulation process are believed to be due to the mild oxidative removal of CO ligands from the starting complex, thus leaving a vacant site for alkene coordination and subsequent cyclisation. From our experience in this area we envisaged that application of an oxidant, such as a suitable amine *N*-oxide, would also promote the formation of the desired pentacarbonyl phosphine complexes. Indeed, following careful optimisation of reaction conditions we have found that trimethylamine *N*-oxide · dihydrate (TMANO · $2H_2O$) efficiently facilitates the formation of the requisite (*R*)-(+)-Glyphos complexes. More specifically, when the alkynehexacarbonyldicobalt compounds are stirred at room temperature in CH_2Cl_2 with 1 molar equivalent of TMANO · $2H_2O$, the pentacarbonyl complexes **5a/b–9a/b** are formed in consistently high yields over short reaction times (Scheme 3, Table 2). Furthermore, these exceedingly mild conditions lead to cleaner reactions with, at most, only trace amounts of the bis-Glyphos complexes being detected.

When the results in both Tables 1 and 2 are considered the diastereomeric ratios observed are also worth



Scheme 3.

noting. Under thermal conditions (Table 1) formation of complexes **5a/b** and **6a/b** occurred with some diastereoselectivity, albeit minor (60:40 for **5a/b** and 40:60 for **6a/b**), and the remaining complexes were isolated as mixtures of diastereoisomers with ratios approaching 50:50. In contrast, all preparations at room temperature (Table 2) yielded 50:50 mixtures except in the case of complexes **6a/b** where a 58:42 diastereomeric mixture was obtained. This apparent reversal in selectivity suggests that complex **6b** is the thermodynamically preferred complex whereas **6a** is kinetically favoured. A similar argument can be made for complexes **5a/b**. These observations have led us to explore the possibility of complex formation under conditions which would enhance this moderate diastereoselectivity, and these studies are currently underway in our laboratory.

With a range of alkynepentacarbonyl–(*R*)-(+)-Glyphos compounds now readily available, attention was turned to isolation of the optically pure complexes (for use in our Pauson–Khand studies [7]). It was found that separation of the diastereomeric mixtures **5a/b–7a/b** could be achieved efficiently by preparative HPLC, using a normal phase silica column with varying mixtures of methyl–*tert*-butyl ether (MTBE) in heptane. However, despite complexes **8a/b** and **9a/b** being routinely resolved by HPLC on an analytical column, separation has this far proved elusive on a preparative scale.

Following isolation, considerable spectral and optical rotation data has been accumulated and the six single diastereomeric complexes obtained have been fully characterised (see also the Experimental section). As an example, the ^{1}H NMR spectra for each individual compound show clear differences, in particular between the acetylenic proton signals. More specifically, the terminal alkyne hydrogens appear at distinct shifts as doublets due to $^3J_{P-H}$ coupling in the range 3.7–5.4 Hz (Table 3). Additionally, optical rotations of the diastereomerically pure complexes, measured at 589 nm, indicated that the first eluting diastereoisomer (by chromatography) was the (−)-isomer and the second eluting complex the (+)-isomer in every case.

Following our success in preparing the pentacarbonyl–(*R*)-(+)-Glyphos complexes **5a/b–9a/b** using TMANO · $2H_2O$ at room temperature, we attempted to widen the scope of this technique to use with more routine phosphines. In some initial studies this mild *N*-oxide methodology has been applied to reactions with the simple phosphine ligand, triphenylphosphine (L = PPh_3). When the parent hexacarbonyl complexes **1**; R^1 = Ph or CMe_2OH, R^2 = H, and L = CO, were subjected to the established *N*-oxide reaction protocol with PPh_3, the monophosphine complexes **1**; R^1 = Ph, R^2 = H, L = PPh_3 and **1**; R^1 = CMe_2OH, R^2 = H, L = PPh_3, were obtained in 69% (cf. 50%, benzene, 70°C, 3 h; Ref. [2]) and 99% yields respectively. Furthermore, reactions were complete after only 30 min with little or no by-product formation. Additionally, the same complexes, **1**; R^1 = Ph, R^2 = H, L = PPh_3 and **1**; R^1 = CMe_2OH, R^2 = H, L = PPh_3, have been prepared in even more rapid reaction times (5–10 min) and, again, in high yields of 85% and 86% respectively using the alternative promoter brucine *N*-oxide at room temperature. This *N*-oxide has also recently been utilised to promote an enantioselective version of the Pauson–Khand cyclisation in our laboratories [15].

In conclusion, we have shown that alkynepentacarbonyl complexes containing the chiral ligand (*R*)-(+)-Glyphos can be readily synthesised in moderate to good yields under standard thermal reaction conditions. Additionally, novel tertiary amine *N*-oxide promoted reactions have been developed which allow the rapid formation of the same mono-(*R*)-(+)-Glyphos complexes in consistently high yields under remarkably mild conditions and in a controlled and selective fashion. The sets of diastereoisomers formed have also been routinely separated by HPLC to provide a range of optically pure complexes which continue to be utilised in enantioselective versions of the Pauson–Khand cycloaddition. Finally, the amine *N*-oxide techniques have been extended to use in the formation of more standard triphenylphosphine complexes with the reactions again proceeding with greater overall efficiency than the equivalent thermally induced transformations. The methodology described here is now being used extensively in our laboratories for the synthesis of optically pure complexes containing phosphine and other isoelectronic ligands.

Table 2
Formation of (*R*)-(+)-Glyphos containing alkynepentacarbonyldicobalt complexes under trimethylamine *N*-oxide·dihydrate promoted conditions

R^1	R^2	Product	Yield (%)	Diastereomeric ratio [a]
Ph	H	**5a/b**	81	50:50
CMe_2OH	H	**6a/b**	100	58:42
CH_2OH	H	**7a/b**	81	50:50
TMS	H	**8a/b**	80	50:50
TMS	CH_3	**9a/b**	85	50:50

[a] Calculated by HPLC on a Spherisorb analytical column.

Table 3
Selected ^{1}H NMR (250 MHz) data for optically pure complexes **5a/b–7a/b**.

Complex	δ (C–C–H) (ppm)	$^3J_{P-H}$ (Hz)
5a	5.23	3.7
5b	5.22	3.7
6a	5.09	5.4
6b	4.69	5.4
7a	5.19	4.8
7b	5.01	4.8

3. Experimental

3.1. General

All reagents were obtained from commercial suppliers and used without further purification, unless otherwise stated. Ether (Et_2O) and tetrahydrofuran (THF) were distilled from Na/benzophenone and methylene chloride (CH_2Cl_2) distilled from calcium hydride under a nitrogen atmosphere. All other solvents used were distilled prior to use. Chromatographic purifications were performed on silica gel (230–400 mesh) by flash technique. Preparative HPLC was carried out on a Spherisorb™ Si-SB3-9961 column using a Waters 600E system controller and a Waters 484 tunable absorbance detector (at 230 nm). Analytical HPLC was carried out on a Spherisorb S5W analytical column using a Waters 501 HPLC pump and a Waters 484 tunable absorbance detector (at 230 nm). Both HPLC systems employed a Waters 746 data module. All cobalt complexes were stored under nitrogen at or below −20°C and all reactions were performed under a nitrogen atmosphere unless otherwise stated.

^1H and ^{13}C NMR were run on a 250 MHz Bruker WM 250 and a 400 MHz Bruker WM 400 in $CDCl_3$ solutions. Chemical shifts are reported in parts per million downfield relative to tetramethylsilane (δ 0.00); coupling constants are reported in hertz. Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer in CH_2Cl_2 solutions. High resolution mass spectrometry was performed on a Jeol Instruments JMS-AX505HA mass spectrometer system. Mass spectral data is reported as *m/e* (relative intensity). Elemental analysis was carried out on a Carlo Erba 1106 CHN analyser.

3.2. Preparation of (R)-(+)-2,3-O-Isopropylidene-glycerol-1-diphenylphosphine [(R)-(+)-Glyphos] 2

3.2.1. Synthesis of (S)-(+)-1,2-O-isopropylidene-glycerol tosylate 4

To a stirred solution of zinc chloride (49.47 g, 0.36 mol) in acetone (300 ml) was added D-mannitol **3** (36.60 g, 0.2 mol) and the resulting mixture stirred for 2 h at room temperature. After this time chloroform (100 ml) and saturated aqueous salt solution (100 ml) were added and the inorganic layer separated. This layer was then washed with chloroform (2 × 100 ml) and the combined organic phases washed with 5% ammonia (200 ml), dried ($MgSO_4$) and excess solvent removed to give 1,2,5,6-diisopropylidene–D-mannitol as a white solid which was used without further purification.

To a solution of sodium periodate (42.8 g, 0.2 mol) in water (300 ml) was added 1,2,5,6-diisopropylidene–D-mannitol in methanol (200 ml) dropwise. The pH of the solution was then adjusted to 6 by addition of lithium hydroxide (1–2 mg) and the temperature of the reaction kept at 30°C for 15 min. After this time the pH was adjusted to 8 by addition of 5 M KOH solution. The reaction mixture was then cooled, the white solid obtained filtered off, sodium borohydride (11.4 g, 0.3 mol) added to the filtrate and the resulting mixture allowed to stir for 20 min with ice cooling. Hexane (150 ml) was then added followed by sodium chloride (12 g) and the resulting mixture shaken with chloroform (200 ml). The resulting phases were separated and the aqueous phase washed with chloroform (2 × 200 ml), the combined organic layers dried and excess solvent removed under reduced pressure to give a clear oil which was then distilled (38–40°C at 1 mmHg) to give (*S*)-(+)-1,2-O-isopropylideneglycerol [10a] (11.5797 g, 45%). ^1H NMR (250 MHz, $CDCl_3$): δ 1.36 (3H, s, CH_3); 1.43 (3H, s, CH_3); 2.22 (1H, s); 3.59 (1H, m); 3.69 (1H, m); 3.77 (1H, dd, J = 8.2, 6.5); 4.02 (1H, dd, J = 8.2, 6.5); 4.18–4.25 ppm (1H, m). FTIR ν_{max} (CH_2Cl_2): 3463 (br, –OH stretch); 3004, 2927, 2902 cm^{-1} (s, aliphatic).

To an ice cooled solution of (*S*)-(+)-1,2-O-isopropylideneglycerol (5.086 g, 0.039 mol) was added *p*-toluenesulfonyl chloride (14.411 g, 0.076 mol) portionwise over a period of 20 min. The resulting solution was then stirred, with ice cooling, for 2 h and stored at 0°C for a further 22 h. The solution was then diluted with ether (150 ml) and washed with cold dilute HCl (200 ml), water (100 ml), saturated sodium bicarbonate solution (100 ml) and water (100 ml). The organic phase was then dried (Na_2SO_4) and the solvent removed under reduced pressure to give a residue which, on flash chromatography (eluent CH_2Cl_2), gave (*S*)-(+)-1,2-O-isopropylideneglycerol tosylate **4** [10b] (9.808 g, 88%) as a viscous oil. ^1H NMR (250 MHz, $CDCl_3$): δ 1.30 (3H, s, CH_3); 1.34 (3H, s, CH_3); 2.45 (3H, s, Ar–CH_3); 3.77 (1H, dd, J = 8.8, 5.1); 3.93–4.08 (3H, m); 4.27–4.31 (1H, m); 7.35 (2H, d, J = 8.3); 7.80 ppm (2H, d, J = 8.3). FTIR ν_{max} (CH_2Cl_2): 3080, 3055 (s, Ar–CH); 2978, 2953, 2902 (s, aliphatic CH); 1625 cm^{-1} (s, S=O stretch).

3.2.2. Synthesis of (R)-(+)-2,3-O-isopropylidene-glycerol-1-diphenylphosphine [(R)-(+)-Glyphos] 2

To a stirred solution of (*S*)-(+)-1,2-O-isopropylideneglycerol tosylate **4** (553 mg, 1.936 mmol) in toluene was added potassium diphenylphosphide (3.87 ml, 1.936 mmol, 0.5 M solution in THF) dropwise, over a period of 20 min. Once addition was complete the resulting red suspension was filtered through a small pad of silica to give a clear solution which on evaporation of the solvent under reduced pressure gave a clear oil residue. Flash column chromatography (eluent CH_2Cl_2) gave (+)-2,3-O-isopropylideneglycerol-1-diphenylphosphine **2** [10c] (492 mg, 85%) as a viscous oil. ^1H NMR (250 MHz, $CDCl_3$): δ 1.33 (3H, s, CH_3); 1.42 (3H, s, CH_3); 2.23 (1H, dd, J = 13.3, 8.4); 2.58

(1H, dd, $J = 13.3, 5.3$); 3.59 (1H, dd, $J = 8.1, 7.4$); 3.99 (1H, dd, $J = 8.1, 5.7$); 4.10–4.21 (1H, m); 7.34 (6H, m); 7.39–7.49 ppm (4H, m). FTIR ν_{max} (CH_2Cl_2): 3029 (s, Ar–CH); 2953, 2876 (s, aliphatic CH); 1753 cm^{-1}. $[\alpha]_D = +13.1$, $c = 0.06$, EtOH.

3.3. Preparation of alkynepentacarbonyl((R)-(+)-Glyphos)dicobalt complexes

3.3.1. General procedure for the preparation of alkynehexacarbonyldicobalt complexes

Octacarbonyldicobalt was charged to a 50 ml round-bottomed flask with nitrogen flowing through constantly. Distilled petrol (30–40°C) was added and the mixture stirred for 5 min after which time a solution of the alkyne in petrol (30–40°C) was added and the reaction mixture left to stir for 3–4 h. The solvent was then removed under reduced pressure and the crude product purified by flash chromatography. Chromatography solvent systems varied for each complex and are indicated in their preparation.

3.3.2. Preparation of phenylacetylenepentacarbonyl((R)-(+)-Glyphos)dicobalt 5a / b

The general complexation procedure was followed with phenylacetylene (2.2521 g, 0.022 mol), octacarbonyldicobalt (8.54 g, 0.025 mol) and petrol (30–40°C) (25 ml) being used to give phenylacetylenehexacarbonyldicobalt [16] (8.4493 g, 99%) following flash chromatography (eluent petrol (30–40°C)). ^1H NMR (250 MHz, $CDCl_3$): δ 6.38 (1H, s); 7.31–7.37 (3H, m); 7.52–7.56 ppm (2H, m). FTIR ν_{max} (CH_2Cl_2): 3086, 3021 (s, aromatic C–H); 2939, 2858, (aliphatic C–H); 2042, 1863 cm^{-1} (M–CO).

Thermal reaction conditions. To a stirred solution of phenylacetylenehexacarbonyldicobalt (164 mg, 0.423 mmol) in toluene (8 ml) was added (*R*)-(+)-Glyphos **2** (115 mg, 0.383 mmol) as a toluene solution (2 ml), and the resulting mixture heated to 60–70°C for 4 h. After filtration through a small pad of Kieselguhr the excess toluene was removed under reduced pressure. The resulting residue, on flash column chromatography (eluent 4 : 1 petrol (30–40°C)/ether), gave (±)-phenylacetylenepentacarbonyl((*R*)-(+)-Glyphos)dicobalt **5a / b** (0.198 g, 78% of the diastereomeric mixture) as a red oil. ^1H NMR (250 MHz, $CDCl_3$) showed a mixture of the two diastereomeric complexes; see below for the individual spectra of the separated complexes. Analytical HPLC using 100% heptane at 0.7 ml min^{-1} gave separation at 6.66 and 7.42 min respectively; ratio 60 : 40. A second complex elucidated by ^1H NMR to be phenylacetylenetetracarbonyl(bis-(*R*)-(+)-Glyphos)dicobalt (52 mg, 13%) was also isolated following column chromatography. ^1H NMR (250 MHz, $CDCl_3$): δ 1.02 (3H, s, CH_3); 1.12 (3H, s, CH_3); 1.17 (3H, s, CH_3); 1.18 (3H, s, CH_3); 1.52–2.05 (2H, m); 2.09–2.28 (2H, m); 2.66 (1H, m); 2.82 (1H, m); 3.29 (2H, m); 4.00 (2H, m); 4.18 (1H, t, $J = 2.7$); 6.90–7.08 (6H, m); 7.14–7.42 ppm (19H, m).

Trimethylamine N-oxide reaction conditions. To a stirred solution of phenylacetylenehexacarbonyldicobalt (50.5 mg, 0.130 mmol) in dichloromethane (5 ml) was added (*R*)-(+)-Glyphos **2** (48.8 mg, 0.163 mmol) and then trimethylamine *N*-oxide · dihydrate (14.5 mg, 0.131 mmol) in one portion. The resulting solution was stirred at room temperature until reaction was complete (60 min) by TLC (4 : 1 petrol (30–40°C)/ether). The reaction mixture was then filtered through a small pad of Kieselguhr and after evaporation of excess solvent the residue, on flash column chromatography (eluent 4 : 1 petrol (30–40°C)/ether), gave (±)-phenylacetylenepentacarbonyl((*R*)-(+)-Glyphos)dicobalt **5a / b** (69.4 mg, 81% of the diastereomeric mixture) as a red oil. Analytical HPLC using 10% *tert*-butyl methyl ether in heptane gave separation at 11.45 and 12.81 min respectively; ratio 50 : 50.

Separation of diastereoisomers 5a and 5b. Preparative HPLC separation was achieved by using 5% *tert*-butyl methyl ether in heptane as mobile phase at a flow rate of 20 ml min^{-1}, giving retention times for **5a** and **5b** of 6.66 and 7.42 min respectively. Three fractions were collected containing the first diastereoisomer, a diastereomeric mixture and the second diastereoisomer. The solutions obtained were stored under nitrogen until removal of the solvents under reduced pressure. This gave each diastereoisomer in a pure form.

Diastereoisomer **5a**: $(-)_{589}$-phenylacetylenepentacarbonyl((*R*)-(+)-Glyphos)dicobalt [4]. ^1H NMR (250 MHz, $CDCl_3$): δ 1.09 (3H, s); 1.15 (3H, s); 1.90–2.05 (1H, m); 2.23–2.40 (1H, m); 2.80–2.87 (1H, dd, $J =$ 8.0, 1.8); 3.40 (1H, dd, $J = 7.0, 1.8$); 4.02 (1H, m); 5.23 (1H, d, $J = 3.7$); 7.10–7.20 (5H, m); 7.30–7.40 ppm (10H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 25.49, 26.65, 34.93, 69.90 (d, $J = 9$); 71.08, 72.18 (d, $J = 33$); 84.98, 108.79, 127.16, 128.29, 128.45, 128.66, 131.41 (d, $J = 10$); 131.76 (d, $J = 10$); 135.19 (d, $J = 12$); 138.80, 201.64 ppm. FTIR ν_{max}(CH_2Cl_2): 3054 (s, Ar–CH); 2940, 2869 (s, aliphatic CH); 2066, 2008, 1957 cm^{-1} (s, M–CO). $[\alpha]_D = -167$, $c = 0.15$, benzene.

Diastereoisomer **5b**: $(+)_{589}$-phenylacetylenepentacarbonyl((*R*)-(+)-Glyphos)dicobalt [4]. ^1H NMR (250 MHz, $CDCl_3$): δ 1.18 (3H, s); 1.22 (3H, s); 2.06–2.18 (1H, m); 2.23–2.40 (1H, m); 2.88–2.97 (1H, dd, $J =$ 8.0); 3.40 (1H, dd, $J = 7.0$); 4.02 (1H, m); 5.22 (1H, d, $J = 3.7$); 7.10–7.20 (5H, m); 7.30–7.45 ppm (10H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 25.49, 26.65, 35.10 (d, $J = 22$); 70.04 (d, $J = 9$); 71.62, 72.18, 87.60, 109.15, 127.16, 130.0, 130.24, 130.76, 130.82, 132.47 (d, $J = 11$); 132.74 (d, $J = 11$); 136.12 (d, $J = 12$); 139.07, 201.64 ppm. FTIR ν_{max} (CH_2Cl_2): 3054 (s, Ar–CH); 2940, 2869 (s, aliphatic CH); 2066, 2008,

1957 cm^{-1} (s, M–CO). $[\alpha]_D = +170$, $c = 0.15$, benzene.

3.3.3. Preparation of 2-methylbut-3-yne-2-olpentacarbonyl((R)-(+)-Glyphos)dicobalt **6a / b**

The general complexation procedure was followed with 2-methylbut-3-yne-2-ol (0.9878 g, 11.74 mmol), octacarbonyldicobalt (5.24 g, 15.3 mmol) and petrol (30–40°C) being used to give 2-methylbut-3-yne-2-olhexacarbonyldicobalt [17] as a red crystalline solid (3.2262 g, 74%) following flash chromatography (eluent 1 : 1 petrol (30–40°C)/ether). ^1H NMR (250 MHz, $CDCl_3$): δ 1.59 (6H, s, $2 \times CH_3$); 1.78 (1H, s, –OH); 6.04 ppm (1H, s). FTIR ν_{max} (CH_2Cl_2): 3627 (s, O–H stretch); 2982 (s, aliphatic C–H); 2113, 2039, 1989 cm^{-1} (s, M–CO).

Thermal reaction conditions. To a stirred solution of 2-methylbut-3-yne-2-olhexacarbonyldicobalt (195 mg, 0.54 mmol) in toluene (8 ml) was added, as a toluene solution (2 ml), (*R*)-(+)-Glyphos **2** (162 mg, 0.54 mmol). The resulting mixture was heated to 60–70°C for 4 h. After filtration through a small pad of Kieselguhr the toluene was removed under reduced pressure. The resulting residue, after flash chromatography (eluent 1 : 1 cyclohexane/ether), gave (±)-2-methylbut-3-yne-2-olpentacarbonyl((*R*)-(+)-Glyphos)dicobalt **6a / b** as a red oil (346 mg, 100%). ^1H NMR (250 MHz, $CDCl_3$) showed a mixture of the two diastereomeric complexes; see below for the individual spectra of the separated complexes. Analytical HPLC using 25% MTBE/heptane gave separation at 5.55 and 6.76 min respectively; ratio 40 : 60.

Trimethylamine N-oxide reaction conditions. To a stirred solution of 2-methylbut-3-yne-2-olhexacarbonyldicobalt (36.3 mg, 0.098 mmol) in dichloromethane (4 ml) was added (*R*)-(+)-Glyphos **2** (36.8 mg, 0.123 mmol) also as a dichloromethane solution (1 ml). To this mixture was added, in one portion, trimethylamine *N*-oxide · dihydrate (11 mg, 0.098 mmol) and the resulting solution stirred at room temperature until reaction was complete (30 min) by TLC (1 : 1 petrol (30–40°C)/ether). The reaction mixture was then filtered through a small pad of Kieselguhr and, after evaporation of excess solvent, the residue obtained gave, on flash chromatography (eluent 1 : 1 petrol (30–40°C)/ether), (±)-2-methylbut-3-yne-2-olpentacarbonyl((*R*)-(+)-Glyphos)dicobalt **6a / b** (62.9 mg, 100%) as a red oil. Analytical HPLC using 35% *tert*-butyl methyl ether in heptane gave separation at 9.65 and 12.56 min respectively; ratio 58 : 42.

Separation of diastereoisomers 6a and 6b. Preparative HPLC separation was achieved using 25% *tert*-butyl methyl ether in heptane as mobile phase at a flow rate of 20 ml min^{-1}, giving retention times for **6a** and **6b** of 11.10 and 14.50 min respectively. Three fractions were collected containing the first diastereoisomer, a diastereomeric mixture and the second diastereoisomer. The solutions obtained were stored under nitrogen until removal of the solvents under reduced pressure. This gave each diastereoisomer in a pure form.

Diastereoisomer **6a**: $(-)_{589}$-2-methylbut-3-yne-2-olpentacarbonyl((*R*)-(+)-Glyphos)dicobalt. ^1H NMR (250 MHz, $CDCl_3$): δ 1.19 (3H, s, CH_3); 1.28 (3H, s, CH_3); 1.38 (3H, s, CH_3); 1.42 (3H, s, CH_3); 1.62 (1H, s, OH); 2.30–2.50 (1H, m); 2.87–3.00 (1H, m); 3.14 (1H, t, $J = 8.1$); 3.49 (1H, dd, $J = 7.0$, 1.8); 4.12 (1H, m); 5.09 (1H, d, $J = 5.4$); 7.34–7.80 ppm (10H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 25.65, 26.84, 32.19, 33.97, 36.51 (d, $J = 23$); 66.07, 70.19, 71.59, 72.51, 73.03, 109.24, 128.84, 128.97, 130.35, 130.69, 132.06 (d, $J = 10$); 132.53 (d, $J = 11$); 135.26 (d, $J = 12$); 201.86 ppm. FTIR ν_{max} (CH_2Cl_2): 3369 (br, –OH); 2957, 2843 (s, aliphatic CH); 2060, 2005, 1957 cm^{-1} (M–CO). Mass spectrum *m/z*: 642.0111 (M^+), 586.0477 ($M^+ - 56$), 530.0735 ($M^+ - 112$), 502.0705 ($M^+ - 140$). Anal. Found: C, 52.09; H, 4.50. Calc.: C, 52.35; H, 4.55%. $[\alpha]_D = -168$, $c = 0.25$, benzene.

Diastereoisomer **6b**: $(+)_{589}$-2-methylbut-3-yne-2-olpentacarbonyl((*R*)-(+)-Glyphos)dicobalt. ^1H NMR (250 MHz, $CDCl_3$): δ 1.30 (3H, s, CH_3); 1.46 (3H, s, CH_3); 1.48 (3H, s, CH_3); 1.60 (3H, s, CH_3); 1.81 (1H, s, OH); 2.22–2.39 (1H, m); 2.84–2.97 (1H, m); 3.26 (1H, t, $J = 8.1$); 3.63 (1H, dd, $J = 7.0$, 1.9); 3.84 (1H, m); 4.69 (1H, d, $J = 5.4$); 7.34–7.80 ppm (10H, m). ^{13}C NMR (62.9 MHz): δ 25.82, 26.91, 32.74, 33.09, 35.33 (d, $J = 20$); 66.07, 70.49, 71.58, 72.51, 73.34, 110.08, 128.74, 129.18, 130.82, 131.04, 133.46 (d, $J = 10$); 134.49 (d, $J = 11$); 138.18 (d, $J = 12$); 201.86 ppm. FTIR ν_{max}(CH_2Cl_2): 3369 (br, –OH), 2957, 2843 (s, aliphatic CH), 2060, 2005, 1957 cm^{-1} (M–CO). Mass spectrum *m/z*: 642.0101 (M^+), 586.1758 ($M^+ - 56$), 530.1676 ($M^+ - 112$), 502.1622 ($M^+ - 140$). Anal. Found: C, 51.89; H, 4.49. Calc.: C, 52.35; H, 4.55%. $[\alpha]_D = +172$, $c = 0.25$, benzene.

3.3.4. Preparation of 1-hydroxyprop-2-ynepentacarbonyl((R)-(+)-Glyphos)dicobalt **7a / b**

The general complexation procedure was followed with 1-hydroxyprop-2-yne (1.00 g, 0.018 mol), octacarbonyldicobalt (7.79 g, 0.022 mol) and petrol (30–40°C) (25 ml) being used to give 1-hydroxyprop-2-ynehexacarbonyldicobalt [16] as a red crystalline solid (5.3819 g, 88%) following flash chromatography (eluent 1 : 1 petrol (30–40°C)/ether). ^1H NMR (250 MHz, $CDCl_3$): δ 1.90 (1H, t, $J = 6.2$, –OH); 4.80 (2H, dd, $J = 5.3$, 0.9); 6.08 ppm (1H, s). FTIR ν_{max} (CH_2Cl_2): 3582 (s, O–H stretch); 2990, 2876 (s, aliphatic C–H); 2110, 2029, 1989 cm^{-1} (s, M–CO).

Thermal reaction conditions. To a stirred solution of 1-hydroxyprop-2-ynehexacarbonyldicobalt (182 mg, 0.543 mmol) in toluene (8 ml) was added (*R*)-(+)-Glyphos **2** (163 mg, 0.543 mmol) as a toluene solution

(2 ml). The resulting mixture was heated to 60–70°C for 4 h. After filtration through a small pad of Kieselguhr the toluene was removed under reduced pressure. The residue obtained, after flash chromatography (eluent 1:1 cyclohexane/ether), gave (±)-1-hydroxyprop-2-ynepentacarbonyl((*R*-(+)-Glyphos)dicobalt **7a/b** as a red oil (277 mg, 83%). ^{1}H NMR (250 MHz, $CDCl_3$) showed a mixture of the two diastereomeric complexes; see below for the individual spectra of the separated complexes. Analytical HPLC using 1% iso-propylalcohol heptane gave separation at 9.03 and 9.85 min respectively; ratio 49:51. A second product elucidated by ^{1}H NMR to be 1-hydroxyprop-2-ynetetracarbonyl(bis-(*R*)-(+)-Glyphos)dicobalt (81 mg, 12%) was also isolated following column chromatography. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.04 (3H, s, CH_3); 1.12 (3H, s, CH_3); 1.18 (3H, s, CH_3); 1.19 (3H, s, CH_3); 2.05 (1H, m, OH); 2.28–2.35 (2H, m); 2.63 (2H, m); 3.06–3.15 (2H, m); 3.42–3.54 (3H, m); 4.16–4.25 (4H, m); 7.27–7.52 ppm (20H, m). FTIR ν_{max}(CH_2Cl_2): 3591 (br, OH); 3080, 3055 (s, aliphatic C–H); 2034, 1982 cm^{-1} (s, M–CO).

Trimethylamine N-oxide reaction conditions. To a stirred solution of 1-hydroxyprop-2-ynehexacarbonyldicobalt (76 mg, 0.222 mmol) in dichloromethane (5 ml) was added (*R*)-(+)-Glyphos **2** (74.1 mg, 0.247 mmol) also as a dichloromethane solution (2 ml). To this mixture was added, in one portion, trimethylamine *N*-oxide · dihydrate (25 mg, 0.225 mmol) and the resulting solution stirred at room temperature until reaction was complete (30 min) by TLC (1:1 petrol (30–40°C)/ether). The reaction mixture was then filtered through a small pad of Kieselguhr and after evaporation of excess solvent the residue obtained gave, on flash chromatography (eluent 1:1 petrol (30–40°C)/ether), (±)-1-hydroxyprop-2-ynepentacarbonyl((*R*)-(+)-Glyphos)dicobalt **7a/b** as a red oil (111 mg, 81%). Analytical HPLC using 35% *tert*-butyl methyl ether in heptane gave separation at 12.21 and 14.85 min respectively; ratio 50:50.

Separation of diastereoisomers 7a and 7b. Preparative HPLC separation was achieved using 35% *tert*-butyl/methyl ether in heptane as mobile phase at a flow rate of 20 ml min^{-1}, giving retention times for **7a** and **7b** of 8.50 and 10.50 min respectively. Three fractions were collected containing the first diastereoisomer, a diastereomeric mixture and the second diastereoisomer. The solutions obtained were stored under nitrogen until removal of the solvents under reduced pressure. This gave each diastereoisomer in a pure form.

Diastereoisomer **7a**: $(-)_{589}$-1-hydroxyprop-2-ynepentacarbonyl((*R*)-(+)-Glyphos)dicobalt. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.25 (3H, s, CH_3); 1.35 (3H, s, CH_3); 1.98 (1H, t, $J = 6.2$); 2.42 (1H, m); 2.70 (1H, m); 3.21 (1H, t, $J = 8.1$); 3.66 (1H, dd, $J = 7.1$, 2.0); 3.98 (2H, m); 4.22 (1H, m); 5.19 (1H, d, $J = 4.8$); 7.34–7.62 ppm (10H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 25.53, 26.75, 29.89, 36.97 (d, $J = 23$); 62.96, 70.21 (d, $J = 8$); 72.08 (d, $J = 31$); 92.55, 109.37, 128.84, 128.99, 129.12, 130.38, 131.24 (d, $J = 11$); 131.80 (d, $J = 11$); 134.43 (d, $J = 12$); 201.76 ppm. FTIR ν_{max} (CH_2Cl_2): 3316 (br, –OH); 2967, 2891 (s, aliphatic CH); 2056, 2003, 1949 cm^{-1} (M–CO). Mass spectrum *m/z*: 614.0113 (M^+), 596.9986 ($M^+ - 18$), 558.0152 ($M^+ - 56$), 502.0541 ($M^+ - 112$), 474.0870 ($M^+ - 140$). Anal. Found: C, 51.06; H, 4.13. Calc.: C, 50.83; H, 4.10%. $[\alpha]_D = -154$, $c = 0.15$, benzene.

Diastereoisomer **7b**: $(+)_{589}$-1-hydroxyprop-2-ynepentacarbonyl((*R*)-(+)-Glyphos)dicobalt. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.26 (3H, s, CH_3); 1.35 (3H, s, CH_3); 1.98 (1H, t, $J = 6.2$); 2.40 (1H, m); 2.70 (1H, m); 3.21 (1H, t, $J = 8.1$); 3.66 (1H, dd, $J = 7.1$, 2.0); 3.80 (2H, m); 4.22 (1H, m); 5.01 (1H, d, $J = 4.8$); 7.34–7.62 ppm (10H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 25.60, 26.75, 30.53, 36.32 (d, $J = 23$); 62.96, 70.39 (d, $J = 8$); 72.08 (d, $J = 31$); 92.55, 109.74, 129.12, 130.38, 130.50, 130.93, 132.37 (d, $J = 10$); 132.82 (d, $J = 10$); 136.37 (d, $J = 12$); 201.76 ppm. FTIR ν_{max} (CH_2Cl_2): 3316 (br, –OH); 2967, 2891 (s, aliphatic CH); 2056, 2003, 1949 cm^{-1} (M–CO). Mass spectrum *m/z*: 613.9194 (M^+), 558.0204 ($M^+ - 56$). Anal. Found: C, 51.01; H, 4.18. Calc.: C, 50.83; H, 4.10%. $[\alpha]_D = +156$, $c = 0.15$, benzene.

3.3.5. *Preparation of 1-trimethylsilylacetylenepentacarbonyl((R)-(+)-Glyphos)dicobalt* **8a/b**

The general complexation procedure was followed with 1-trimethylsilylacetylene (168 mg, 1.171 mmol), octacarbonyldicobalt (648.9 mg, 1.89 mmol) and petrol (30–40°C) (10 ml) giving 1-trimethylsilylacetylenehexacarbonyldicobalt [18] (0.696 g, 100%) as a red oil following flash chromatography (eluent petrol (30–40°C)). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.30 (9H, s, $(CH_3)_3Si$–); 6.38 ppm (1H, s). FTIR ν_{max} (CH_2Cl_2): 2982, 2907 (s, aliphatic C–H); 2113, 2039, 1989 cm^{-1} (s, M–CO).

Thermal reaction conditions. To a stirred solution of 1-trimethylsilylacetylenehexacarbonyldicobalt (194 mg, 0.471 mmol) in toluene (4 ml) was added (*R*)-(+)-Glyphos **2** (141 mg, 0.471 mmol) as a toluene solution (1 ml). The resulting mixture was heated to 60–70°C for 4 h. After filtration through a small pad of Kieselguhr the toluene was removed under reduced pressure and the resulting residue, after flash chromatography (eluent 1:1 cyclohexane/ether), gave (±)-1-trimethylsilylacetylenepentacarbonyl((*R*)-(+)-Glyphos)dicobalt **8a/b** as a red oil (220 mg, 68%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.06 and 0.08 (9H, 2 × s); 1.14 and 1.16 (3H 2 × s, CH_3); 1.19 and 1.21 (3H, 2 × s, CH_3); 2.27 (1H, m); 2.60 (1H, m); 2.96 (1H, m); 3.41 (1H, m); 4.10 (1H, m); 5.35 (1H, 2 × d, $J = 6.2$); 7.28–7.50 ppm (10H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 1.73, 25.59, 26.85, 37.27 (d, $J = 23$); 69.93, 72.51, 73.34 (d,

$J = 21$); 85.26, 85.53, 108.99, 109.04, 128.64, 128.78, 128.91, 130.28, 130.61, 130.74, 131.84 (d, $J = 10$); 132.08 (d, $J = 10$); 132.24 (d, $J = 10$); 132.58 (d, $J = 10$); 134.92 (d, $J = 10$); 135.96 (d, $J = 10$); 202.29 ppm. FTIR ν_{max} (CH_2Cl_2): 2987, 2881 (s, aliphatic CH); 2060, 2005, 1957 cm^{-1} (M–CO). Mass spectrum m/z: 655.9976 (M^+), 599.9810 ($M^+ - 56$), 544.0029 ($M^+ - 112$), 516.0094 ($M^+ - 140$). Anal. Found: C, 51.40; H, 4.82. Calc.: C, 51.20; H, 4.72%. Analytical HPLC using 5% *tert*-butyl methyl ether in heptane at a flow rate of 0.7 ml min^{-1} gave separation at 11.66 and 12.33 min respectively; ratio 49:51.

Trimethylamine N-oxide conditions. To a stirred solution of 1-trimethylsilylacetylenehexacarbonyldicobalt (54.5 mg, 0.142 mmol) in dichloromethane (4 ml) was added (*R*)-(+)-Glyphos **2** (43.6 mg, 0.145 mmol) also as a dichloromethane solution (1 ml). To this mixture was added, in one portion, trimethylamine *N*-oxide · dihydrate (15.6 mg, 0.145 mmol) and the resulting solution stirred at room temperature until reaction was complete (60 min) by TLC (1 : 1 petrol (30–40°C)/ether). The reaction mixture was then filtered through a small pad of Kieselguhr and, after evaporation of excess solvent, the residue obtained gave, on flash chromatography (eluent 1 : 1 petrol (30–40°C)/ether), (±)-1-trimethylsilylacetylenepentacarbonyl((*R*)-(+)-Glyphos)dicobalt **8a/b** as a red oil (74.7 mg, 80%). Analytical HPLC using 5% *tert*-butyl methyl ether in heptane at a flow rate of 0.7 ml min^{-1} gave separation at 11.24 and 11.98 min respectively; ratio 50:50.

*Attempted separation of diastereoisomers **8a** and **8b**.* Preparative HPLC of the diastereomeric mixture was attempted using 5% *tert*-butyl methyl ether in heptane as mobile phase, however separation of the diastereoisomers was not achieved.

3.3.6. Preparation of 1-(trimethylsilyl)-1-propynepentacarbonyl((R)-(+)-Glyphos)dicobalt 9a/b

The general complexation procedure was followed with 1-(trimethylsilyl)-1-propyne (1.0439 g, 9.299 mmol), octacarbonyldicobalt (3.19 g, 9.327 mmol) and petrol (30–40°C) (10 ml) being used to give, after flash chromatography (eluent petrol (30–40°C)), 1-(trimethylsilyl)-1-propynehexacarbonyldicobalt [19] as a red oil (3.734 g, 96%). ^1H NMR (250 MHz, $CDCl_3$): δ 0.31 (9H, s, $(CH_3)_3Si$–); 2.74 ppm (3H, s, CH_3). FTIR ν_{max} (CH_2Cl_2): 2984, 2925 (s, aliphatic C–H); 2110, 2036, 1987 cm^{-1} (s, M–CO).

Thermal reaction conditions. To a stirred solution of 1-(trimethylsilyl)-1-propynehexacarbonyldicobalt (98 mg, 0.229 mmol) in toluene (8 ml) was added (*R*)-(+)-Glyphos **2** (66 mg, 0.220 mmol) as a toluene solution (2 ml). The resulting mixture was heated to 60–70°C for 4 h. After filtration through a small pad of Kieselguhr the toluene was removed under reduced pressure. The resulting residue, after flash chromatography (eluent 1 : 1 cyclohexane/ether), gave 1-(tri-methylsilyl)-1-propynepentacarbonyl((*R*)-(+)-Glyphos)dicobalt **9a/b** as a red oil (67 mg, 48%) and recovered starting material (26 mg, 27%), i.e. yield of 57% based on recovered starting material. ^1H NMR (250 MHz, $CDCl_3$): δ 0.09 and 0.10 (9H, 2 × s); 1.10–1.62 (6H, m, 2 × CH_3); 1.78 (3H, s, CH_3); 2.24 (1H, m); 2.60 (1H, m); 2.79 (1H, 2 × d, $J = 8.2$); 3.26 (1H, m); 4.02 (1H, m); 7.22–7.50 ppm (10H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 1.73, 19.77, 25.53, 26.77, 37.59, 37.83, 38.17, 69.74, 72.48, 104.46, 108.76, 108.94, 128.74, 128.88, 130.30, 130.67, 130.81, 131.84 (d, $J = 10$); 132.08 (d, $J = 10$); 132.24 (d, $J = 10$); 132.58 (d, $J = 10$); 134.92 (d, $J = 10$); 135.96 (d, $J = 10$); 202.29 ppm. FTIR ν_{max} (CH_2Cl_2): 2988, 2871 (s, aliphatic CH); 2055, 2001, 1953 cm^{-1} (M–CO). Mass spectrum m/z: 670.0135 (M^+), 614.0185 ($M^+ - 56$), 558.0263 ($M^+ - 112$), 530.0388 ($M^+ - 140$). Anal. Found: C, 51.83; H, 4.99. Calc.: C, 51.92; H, 4.92%. Analytical HPLC using 5% *tert*-butyl methyl ether in heptane at a flow rate of 0.7 ml min^{-1} gave separation at 10.27 and 11.36 min respectively; ratio 51:49.

Trimethylamine N-oxide conditions. To a stirred solution of 1-(trimethylsilyl)-1-propynehexacarbonyldicobalt (114 mg, 0.286 mmol) in dichloromethane (4 ml) was added (*R*)-(+)-Glyphos **2** (89.3 mg, 0.297 mmol) also as a dichloromethane solution (1 ml). To this mixture was added, in one portion, trimethylamine *N*-oxide · dihydrate (33 mg, 0.297 mmol) and the resulting solution stirred at room temperature until reaction was complete (60 min) by TLC (10 : 1 petrol (30–40°C)/ether). The reaction mixture was then filtered through a small pad of Kieselguhr and, after evaporation of excess solvent, the residue obtained gave, on flash chromatography (eluent 10 : 1 petrol (30–40°C)/ether), (±)-1-(trimethylsilyl)-1-propynepentacarbonyl((*R*)-(+)-Glyphos)dicobalt **9a/b** as a red oil (162 mg, 85%). Analytical HPLC using 5% *tert*-butyl methyl ether in heptane at a flow rate of 0.7 ml min^{-1} gave separation at 10.67 and 11.46 min respectively; ratio 50:50.

*Attempted separation of diastereoisomers **9a** and **9b***
Preparative HPLC of the diastereomeric mixture was attempted using 5% *tert*-butyl methyl ether in heptane as mobile phase, however separation of the diastereoisomers was not achieved.

3.4. Preparation of alkynepentacarbonyl(triphenylphosphine)dicobalt complexes

3.4.1. Preparation of phenylacetylenepentacarbonyl(triphenylphosphine)dicobalt 1: $R^1 = Ph$, $R^2 = H$, $L = PPh_3$

Trimethylamine N-oxide reaction conditions. To a stirred solution of phenylacetylenehexacarbonyldicobalt

(59.4 mg, 0.153 mmol) in dichloromethane (5 ml) was added triphenylphosphine (40 mg, 0.153 mmol) and trimethylamine *N*-oxide · dihydrate (17 mg, 0.153 mmol) and the resulting reaction mixture stirred at room temperature. After 30 min TLC (4:1 petrol (30–40°C)/ether) indicated that the reaction was complete and, after filtration through a small pad of Kieselguhr, excess solvent was removed under reduced pressure and the residue, on flash column chromatography (eluent 4:1 petrol (30–40°C)/ether), gave phenylacetylenepentacarbonyl(triphenylphosphine)dicobalt **1**; $R^1 = Ph$, $R^2 = H$, $L = PPh_3$ [2] (65.8 mg, 69%). ^1H NMR (250 MHz, $CDCl_3$): δ 5.46 (1H, d, $J = 3.6$); 7.07–7.25 (14H, m); 7.52–7.55 (3H, m); 7.70–7.72 ppm (3H, m). FTIR ν_{max} (CH_2Cl_2): 3086, 3021 (s, aromatic C–H); 2939, 2858, (aliphatic C–H); 2042, 2005, 1972, 1863 cm^{-1} (M–CO).

Brucine N-oxide reaction conditions. To a stirred solution of phenylacetylenehexacarbonyldicobalt (49.6 mg, 0.128 mmol) in dichloromethane (5 ml) was added triphenylphosphine (33.4 mg, 0.128 mmol) and brucine *N*-oxide (53 mg, 0.129 mmol) and the resulting solution stirred at room temperature until reaction was complete (10 min) as indicated by TLC (4:1 petrol (30–40°C)/ether). Purification, as above, gave phenylacetylenepentacarbonyl(triphenylphosphine)dicobalt **1**; $R^1 = Ph$, $R^2 = H$, $L = PPh_3$ (67.3 mg, 85%).

3.4.2. Preparation of 2-methylbut-3-yne-2-olpentacarbonyl(triphenylphosphine)dicobalt 1; $R^1 = CMe_2OH$, $R^2 = H$, $L = PPh_3$

Trimethylamine N-oxide reaction conditions. To a stirred solution of 2-methylbut-3-yne-2-olhexacarbonyldicobalt (51 mg, 0.138 mmol) in dichloromethane (5 ml) was added triphenylphosphine (39 mg, 0.138 mmol) and trimethylamine *N*-oxide · dihydrate (16 mg, 0.142 mmol) and the resulting reaction mixture stirred at room temperature until reaction was complete (30 min) by TLC (2:1 petrol (30–40°C)). The reaction mixture was then filtered through a small pad of Kieselguhr and, after removal of excess solvent, the residue, on flash column chromatography (eluent 2:1 petrol (30–40°C)/ether), gave 2-methylbut-3-yne-2-olpentacarbonyl(triphenylphosphine)dicobalt **1**; $R^1 = CMe_2OH$, $R^2 = H$, $L = PPh_3$ as a red oil (83 mg, 99%). ^1H NMR (250 MHz, $CDCl_3$): δ 1.26 (1H, s, OH); 1.32 (3H, s, CH_3); 1.45 (3H, s, CH_3); 5.26 (1H, d, $J = 5.5$); 7.34–7.54 ppm (15H, m). FTIR ν_{max} (CH_2Cl_2): 3086, 3061 (s, aromatic C–H); 2929, 2841, (aliphatic C–H); 2089, 2034, 1979 cm^{-1} (M–CO).

Brucine N-oxide reaction conditions. To a stirred solution of 2-methylbut-3-yne-2-olhexacarbonyldicobalt (53.8 mg, 0.146 mmol) in dichloromethane (5 ml) was added triphenylphosphine (38 mg, 0.146 mmol) and brucine *N*-oxide (60 mg, 0.146 mmol) and the resulting solution stirred at room temperature until reaction was complete (5 min) by TLC (2:1 petrol (30–40°C)/ether). Purification, as above, gave 2-methylbut-3-yne-2-olpentacarbonyl(triphenylphosphine)dicobalt **1**; $R^1 = CMe_2OH$, $R^2 = H$, $L = PPh_3$ as a red oil (75.6 mg, 86%).

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References and notes

[1] (a) R.S. Dickson and P.J. Fraser, *Adv. Organomet. Chem., 12* (1974) 323; (b) N.E. Schore, *Chem. Rev., 88* (1988) 1081; (c) K.M. Nicholas, *Acc. Chem. Res., 20* (1987) 207.
[2] L.S. Chai, W.R. Cullen, M. Franklin and A.R. Manning, *Inorg. Chem., 14* (1975) 2521.
[3] (a) M.F. D'Agostino, C.S. Frampton and M.J. McGlinchey, *Organometallics, 9* (1990) 2972; (b) J.A. Dunn and P.L. Pauson, *J. Organomet. Chem., 419* (1991) 383.
[4] P. Bladon, P.L. Pauson, H. Brunner and R. Eder, *J. Organomet. Chem., 355* (1988) 449.
[5] R.F. Heck, *J. Am. Chem. Soc., 85* (1963) 657.
[6] M. Arewgoda, B.H. Robinson and J. Simpson, *J. Am. Chem. Soc., 105* (1983) 1893.
[7] A.M. Hay, W.J. Kerr, G.G. Kirk and D. Middlemiss, *Organometallics, 14* (1995) 4986.
[8] For reviews on the Pauson–Khand reaction see: P.L. Pauson and I.U. Khand, *Ann. New York Acad. Sci., 295* (1977) 2; P.L. Pauson, *Tetrahedron, 41* (1985) 5855; N.E. Schore, *Org. React., 40* (1991) 1; N.E. Schore, in B.M. Trost and I. Fleming (eds.), *Comprehensive Organic Synthesis*, Vol. 5, Pergamon, Oxford, 1991, p. 1037.
[9] J.C. Anderson, B.F. Taylor, C. Viney and G.J. Wilson, *J. Organomet. Chem., 519* (1996) 103.
[10] (a) U. Schmidt, J. Talbiersky, F. Bartkowiak and J. Wild, *Angew. Chem., Int. Ed. Engl., 19* (1980) 198; (b) J.J. Baldwin, A.W.Q. Raab, K. Mensler, B.H. Arison and D.E. McLure, *J. Org. Chem., 43* (1978) 4876; (c) H. Brunner and H. Leyerer, *J. Organomet. Chem., 334* (1987) 369.
[11] Available commercially from Aldrich Chemical Co.
[12] H. Brunner and A. Niedernhuber, *Tetrahedron: Asymm., 1* (1990) 711.
[13] C. Johnstone, W.J. Kerr and U. Lange, *J. Chem. Soc., Chem. Commun.*, (1995) 457; A.R. Gordon, C. Johnstone and W.J. Kerr, *Synlett*, (1995) 1083.
[14] S. Shambayati, W.E. Crowe and S.L. Schreiber, *Tetrahedron Lett., 31* (1990) 5289; N. Jeong, Y.K. Chung, B.Y. Lee, S.H. Lee and S.-E. Yoo, *Synlett*, (1991) 204; Y.K. Chung, B.Y. Lee, N. Jeong, M. Hudecek and P.L. Pauson, *Organometallics, 12* (1993) 220; M.E. Krafft, I.L. Scott, R.H. Romero, S. Feibelmann and C.E. Van Pelt, *J. Am. Chem. Soc., 115* (1993) 7199.
[15] W.J. Kerr, G.G. Kirk and D. Middlemiss, *Synlett*, (1995) 1085.
[16] H. Greenfield, H.W. Sternberg, R.A. Friedel, J.H. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc., 78* (1956) 120.
[17] M.R. Tirpak, C.A. Hollingsworth and J.H. Wotiz, *J. Org. Chem., 25* (1960) 687.
[18] U. Kruerke and W. Hubel, *Chem. Ber., 94* (1961) 2829.
[19] R.S. Dickson and H.P. Kirsch, *Aust. J. Chem., 25* (1972) 1815.