PPh$_3$ under similar mild conditions (90 °C, 5 min) induced the simultaneous removal of two CO ligands and afforded **6a** as the only observed product.[15] Interestingly, heating **5a** under relatively severe condition (110 °C, 10 min) also produced **6a** in 87% yield.

Again, X-ray analysis of **6a** shows that it is generated via ortho-metalation and that the phosphorus atom is no longer attached to the Ru atom carrying the σ-interaction of the alkenyl group.[14] These structural data not only account for the harsh conditions needed for the conversion of **5a** to **6a** but also serve as further evidence to support the characterization of **4a**, as the transformation from **4a** to **6a** involves no alkenyl migration. Furthermore, because the intermediacy of **5a** is nonessential, the transformation from **4a** to **6a** is easier and faster. ·

In addition, if the transformation from **5a** to **6a** requires migration of the alkenyl group in a manner similar to the process demonstrated earlier, it would demand that the PPh$_3$ ligand in **5a** undergoes intermetallic migration on the Ru–Ru edge prior to the occurrence of ortho-metalation. In order to verify this postulate, we have carried out the thermolysis of **5a** in the presence of 1 molar equiv of

PTol$_3$. The addition of PTol$_3$ has no noticeable effect on the rate or the yield of the reaction; however, ^{1}H NMR data showed that the product isolated is a 1:2 mixture of **6a** and its crossover product, the PTol$_3$-substituted complex. This observation suggests that the coordinated PPh$_3$ has dissociated from **5a** and then mixed with free PTol$_3$ in solution before reentry into the coordination sphere. Strictly speaking, this qualitative experiment does not explicitly confirm the dissociative, intermetallic migration, and we tend to believe that phosphine migration is what actually occurred since dissociation is a prerequisite for the proposed process. In contrast, the unlikely alternative involving a reversible π → σ, σ → π alkenyl rearrangement on the Ru–Ru edge[6,7] followed by movement of the alkenyl group to the adjacent W–Ru edge can be ignored because it requires no phosphine dissociation. Attempts to fully delineate the reaction mechanism are currently in progress.

(15) Spectral data are as follows. Complex **6a**: *m/z* (FAB; ^{102}Ru, ^{184}W) 1108.90 (M$^+$); IR (CCl$_4$) ν(CO) 2061 (m), 2039 (vs), 1996 (m), 1990 (m), 1834 (m) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, RT) δ 7.26 (m, 1 H), 7.31–6.05 (m, 18 H), 5.52 (s, 5 H), 2.47 (q, 1 H, J_{F-H} = 10.5 Hz), –17.88 (d, 1 H, J_{P-H} = 15.3 Hz). Anal. Calcd for C$_{38}$H$_{26}$F$_6$NO$_5$PRu$_2$W: C, 41.21; H, 2.37; N, 1.26. Found: C, 38.68; H, 2.29; N, 1.18.

Mechanistic Aspects of the Alternating Copolymerization of Carbon Monoxide with Olefins Catalyzed by Cationic Palladium Complexes

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Summary: The copolymerization of propylene with carbon monoxide using a catalytic system based on palladium acetate, modified with the atropisomeric chiral ligand (*S*)-(6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine), gives poly[spiro-2,5-(3-methyltetrahydrofuran)]. This material is transformed into the isomeric poly(1-oxo-2-methyltrimethylene) by dissolution in hexafluoro-2-propanol and precipitation with methanol. A mechanism based on a carbene intermediate is proposed in order to account for the formation of the polyketone material in the spiroketal form.

Systems of the type (L-L)PdX$_2$ (L-L = monodentate or bidentate phosphorus or nitrogen ligands; X = noncoordinating or weakly coordinating anion) have been found to catalyze the strictly alternating copolymerization of ethylene and carbon monoxide.[1,2] The development of

very active catalytic systems[3] allowed also the production of copolymers of α-olefins such as propylene or 4-methyl-1-pentene. A regioregular enchainment of the olefinic monomeric units for these substrates has been achieved by using bidentate basic sterically demanding diphosphines such as 1,3-propanediylbis(diisopropylphosphine)[4] or 1,3-propanediylbis(dicyclohexylphosphine).[5] Furthermore the use of the chiral ligand (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine) allowed us to synthesize a copolymer showing a quite high stereoregularity, probably of the isotactic type.[5] The achiral catalytic system (1,10-phenanthroline)Pd(p-CH$_3$C$_6$H$_4$SO$_3$)$_2$ catalyzes the highly stereoregular formation of syndiotactic poly(1-oxo-2-phenyltrimethylene).[6-8]

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(1) (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520. (b) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866.

(2) Drent, E. Eur. Pat. Appl. 1984, 121, 965 (*Chem. Abstr.* **1985**, *102*, 46423).

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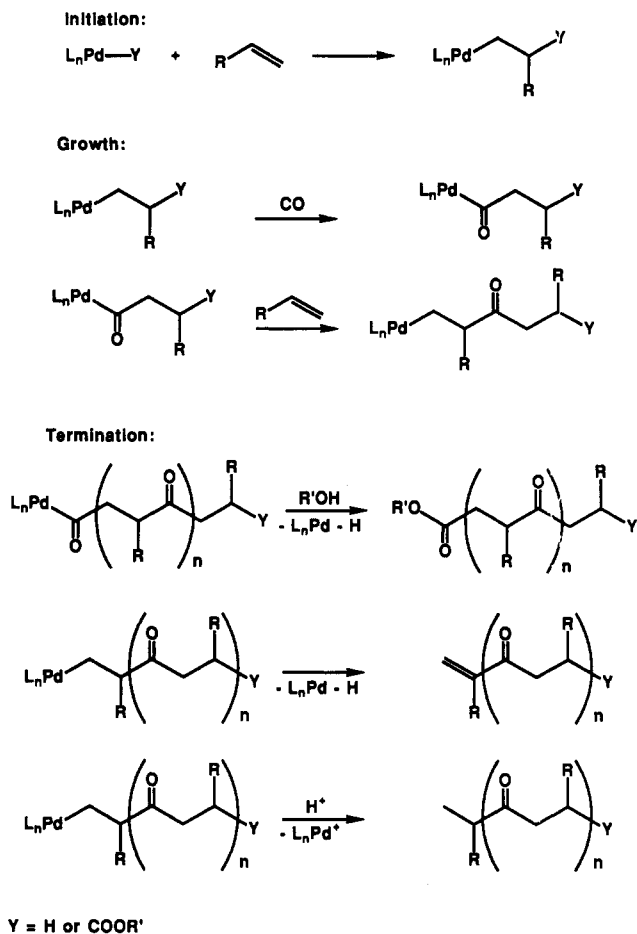(7) Corradini, P.; De Rosa, C.; Panunzi, A.; Petrucci, G.; Pino, P. *Chimia* **1990**, *44*, 52.

(8) Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. W. *Angew. Chem* **1991**, *103*, 992; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989.

Scheme I. Proposed Mechanism for the Copolymerization of Olefins with Carbon Monoxide (with Regioselectivity of the Olefin Insertion Arbitrarily Chosen)

Initiation:

Growth:

Termination:

Y = H or COOR'

Scheme II. Copolymerization of Olefins with Carbon Monoxide: Kinetic and Thermodynamic Products[a]
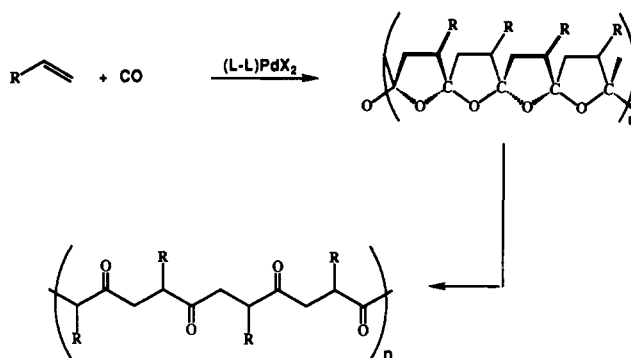
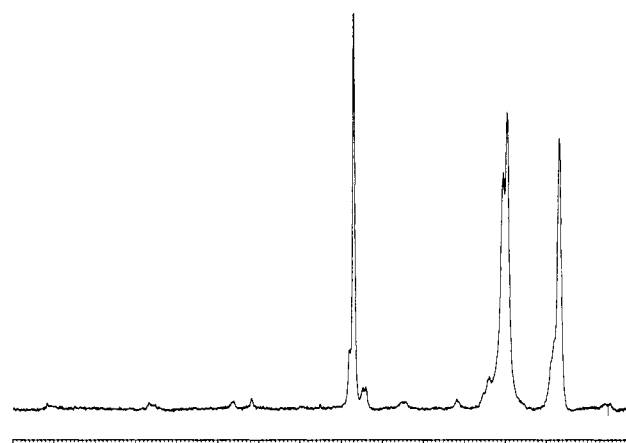[a] The stereochemistry of the spiroketal structure is arbitrary.

Figure 1. ^{13}C-NMR MAS spectrum (100 MHz; Rotor 5000) of an untreated solid copolymer between propylene and carbon monoxide prepared using (S)-(6,6'-dimethylbiphenyl-2,2'-diyl)-bis(dicyclohexylphosphine)/Pd(CH₃COO)₂/NiClO₄ as the catalyst precursor.

According to the analysis of end groups and to the identification of oligomeric compounds formed during the copolymerization process the following mechanism[3,8,9] for the formation of the copolymers has been proposed (Scheme I): (i) Initiation takes place through insertion of an olefin unit into a metal–hydride or into a metal–carb-alkoxy bond. (ii) The growing steps consist of insertions of carbon monoxide units into a metal–alkyl bond and of olefin units into a metal–acyl bond. (iii) Termination takes place through alcoholysis of a metal–acyl bond, through β-hydrogen elimination from, or through protonolysis of, a metal–alkyl species. The latter termination was not observed in the formation of the styrene copolymer.[8]

Indeed, this description is a mere adaptation of the proposed mechanisms of other well-known carbonylation reactions such as hydroformylation[10] and hydrocarbalkoxylation[10,11] to the copolymerization process.

This mechanism is *not consistent* with the structure of the product formed, at least when aliphatic α-olefins or cyclic olefins are the substrate. In fact, it has been reported first for propylene[12] and then for cyclic olefins[13] that the recovered copolymer can show, at least in part, a spiroketal

structure. The polyketone structure represents the thermodynamically more stable form (Scheme II);[12] from a kinetic point of view, however, the spiroketal structure must be accounted for.

In Figure 1 the ^{13}C-NMR MAS spectrum of the solid copolymer between propylene and carbon monoxide just as formed is reported; this copolymer was obtained using a palladium catalyst of the aforementioned type modified with the chiral ligand (S)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine).[14] Instead of a band attributable to the carbonyl groups (δ ~220 ppm) a strong band in the region of ketal groups (>C(OR)₂) (δ 113 ppm)[15] is present. By contrast, in the ^{13}C-NMR spectrum of the same sample dissolved in hexafluoro-2-propanol only the signals attributable to carbonyl groups (δ ~219 ppm) in

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(11) Milstein, D. *Acc. Chem. Res.* 1988, *21*, 428.

(12) Van Doorn, J. A.; Wong, P. K.; Sudmeier, O. Eur. Pat. Appl. 1989, 376,364 (*Chem. Abstr.* 1991, *114*, 24797).

(13) Drent, E. Eur. Pat. Appl. 1990, 399,617 (*Chem. Abstr.* 1991, *114*, 165108).

(14) The copolymer was prepared as follows: A solution of (S)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine) (40 mg, 0.07 mmol), 1,4-naphthoquinone (475 mg, 3 mmol), Ni(ClO₄)₂·6H₂O (111 mg, 0.3 mmol), and Pd(CH₃COO)₂ (13.5 mg, 0.06 mmol) in 151.5 mL of tetrahydrofuran and 8.5 mL of methanol was introduced in a stainless steel 0.5-L autoclave under nitrogen, followed by 39 g of propylene. The autoclave was heated up to 42 °C and pressurized with 80 bar of carbon monoxide. After 213 h at that temperature the autoclave was cooled down and the pressure was slowly released. To the white suspension was added 200 mL of methanol, and the resulting mixture was allowed to decant at 5 °C for 2 days. The copolymer (10.1 g) was recovered by filtration, washed with methanol, and dried at room temperature in vacuum (mp 264 °C; MW ~3000 (estimated from NMR)). After evaporation of the solvent from the filtrate 3 g of oligomers was recovered.

(15) For ^{13}C-NMR chemical shifts of spiroketal compounds, see, e.g.: Brimble, M. A.; Williams, G. M.; Baker, R. *J. Chem. Soc., Perkin Trans. 1* 1991, 2221.

Scheme III. Proposed New Mechanism for the Copolymerization of Olefins with Carbon Monoxide (with Regioselectivity of the Olefin Insertion Arbitrarily Chosen)

Scheme IV. Possible Pathway for the Formation of a Carbene Intermediate during the Copolymerization of Olefins with Carbon Monoxide
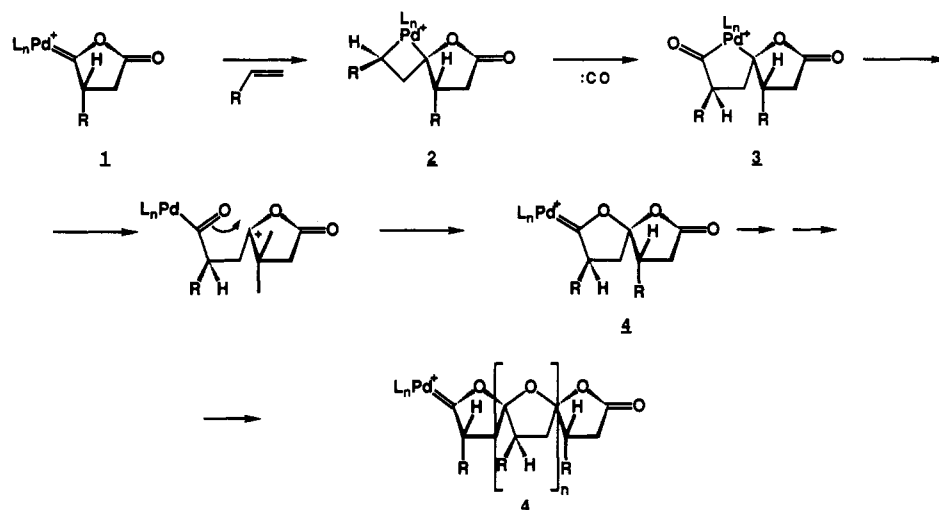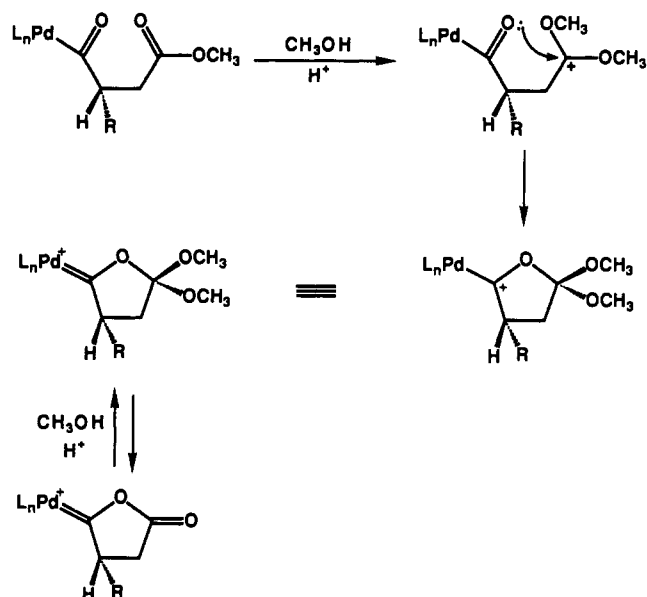

addition to those corresponding to the olefin carbon atoms can be detected.

Consistently, the IR spectrum of the solid untreated sample in the KBr pill shows only two very small bands in the region of the carbonyl stretching (1708 and 1743 cm⁻¹); in addition there are some medium bands in the region 1300–1000 and one at 840 cm⁻¹ (attributable to C–O–C asymmetric stretching). When the copolymer is dissolved in hexafluoro-2-propanol and reprecipitated with methanol a very strong band at 1708 cm⁻¹ appears whereas the bands at lower wavenumbers disappear.

To explain the formation of poly(1-oxo-2-methyltrimethylene) in the spiroketal structure, a *different mechanistic picture* must be sought. Although we do not have at the moment any detailed mechanistic study of the reaction, we would like to propose as a work hypothesis that the chain is propagated by carbene species (Scheme III, 1 and 4). A possible[16] pathway for the formation of species 1 is proposed in Scheme IV. This proposal would also give a rationale for the positive effect of the presence of methyl orthoformate on the copolymerization rate.[19] The probable presence of lactone end groups is inferred by the signal at 1743 cm⁻¹ in the IR spectrum and by the low-intensity signal at ~173 ppm in the ¹³C-NMR MAS spectrum (Figure 1). The possible existence of carbene species under the reaction conditions used is strongly suggested by previously reported results in platinum chemistry.[17,18] Moreover, the steps related to the formation of intermediates 2 and 3 (Scheme III) have recently been discussed in the field of the chromium carbene complexes.[20] Termination reactions can take place at the level of intermediate 4, e.g., with formation of a ketene species and eventually of a carboalkoxy end group.[21] Alternatively, termination at the level of intermediate 2 could lead to the formation of unsaturated end groups.[22]

The poly(1-oxo-2-methyltrimethylene) derived from the poly[spiro-2,5-(3-methyltetrahydrofuran)] of Figure 1 shows a quite high stereoregularity.[5] The stereochemistry of the spiro stereogenic units is at the moment unknown; however, the narrowness of the band at 113 ppm (Figure 1) might imply a high atropoisomeric regularity. The very interesting question arises about the possible existence of a mutual interdependence between centers and axes of chirality and about the role of the spiro stereogenic units on the stereochemistry of the produced polyketones.

Due to the thermodynamic instability of the spiroketal structure the mechanism leading to this structure during the formation of the polyketone copolymers might have a broad generality for the aforementioned $(L-L)PdX_2$ catalytic systems. The stereogenic carbene moiety implied in the mechanism proposed in this paper (Scheme III) could, in fact, give a better rationale than the classical mechanism (Scheme I) for the large enantioface selection during the copolymerization of styrene and carbon monoxide to highly syndiotactic poly(1-oxo-2-phenyltrimethylene) using the achiral (1,10-phenanthroline)Pd(p-$CH_3C_6H_4SO_3$)$_2$ catalyst precursor.[6-8]

(16) Other alternatives can be envisaged, e.g., compare refs 17 and 18 and: Yang, G.-M.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1991**, 478.

(17) Chisolm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202.

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(19) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Wong, P. K. Eur. Pat. Appl. **1989**, 393,790 (*Chem. Abstr.* **1991**, *114*, 103034).

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(22) Compare ref 21, pp 459–520.

The remarkable finding of kinetic and thermodynamic structures for the copolymers between olefins and carbon monoxide[12,13] will surely awake new interest and stimulate research in the apparently neglected subject[17,18] of cationic carbene complexes of platinum and palladium.

Bis(fluorenyl)barium–Tetrakis(ammonia), The First Structurally Characterized Alkaline-Earth-Metal Fluorenyl Complex. Are BaX₂ Structures Inherently Bent?

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Summary: Reaction of 2 equiv of fluorene with barium in liquid ammonia provides the orange air- and moisture-sensitive $(C_{13}H_9)_2Ba(NH_3)_4$ (1) in 87% yield. The X-ray structure of crystalline 1 reveals two different monomeric conformers exhibiting bent-sandwich structures with an average Ba–C distance of 2.94 Å to the five-membered rings of the fluorenyl anion moieties and ring centroid–Ba–ring centroid angles of 112.3 and 116.4°. Four ammonia molecules complete the coordination sphere of barium. This supports the general preference of $BaX_2 \cdot L_n$ compounds (X = anionic ligand, L = neutral ligand) for bent rather than linear arrangements of the $X^- Ba^{2+} X^-$ moieties.

Alkaline-earth-metal compounds are dominated by their highly ionic character. Due to their involatility and insolubility in common organic solvents, only a few derivatives of "true" calcium, strontium, and barium organometallics have been investigated.[1] $Ba(Me_5C_5)_2$, the first structurally characterized organobarium complex,[2] has a "quasipolymeric" structure with bent metallocenes (the ring centroid–metal–ring centroid angle is 131°). A similar structure was obtained for $[(C_3H_7)_4C_5H]_2Ba.$[3] Here, two crystallographically independent but nearly identical molecules are present in the asymmetric unit. The ring centroid–metal–ring centroid angle of 154.3° is significantly larger than that in $Ba(Me_5C_5)_2$.

We now report on the X-ray structure of bis(fluorenyl)barium–tetrakis(ammonia) (1), the first X-ray structure of an alkaline-earth-metal fluorene complex. In solution, $Ba(Fl)_2$ (Fl = fluorene) has been studied by electronic, spectroscopic, and conductometric methods.[4] Absorption and emission spectra were interpreted to suggest the existence of triple ion pairs with mutually tilted fluorenyl units. This feature would allow additional ex-
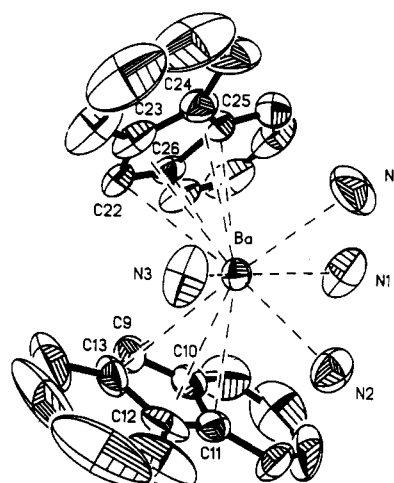

Figure 1. Ortep plot for bis(fluorenyl)barium–tetrakis(ammonia) (1), giving the numbering scheme used in Table I.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 1A and 1B

	1A	1B
Bond Lengths		
Ba–C9	3.151	3.107
Ba–C10	3.180	3.099
Ba–C11	3.189	3.098
Ba–C12	3.171	3.120
Ba–C13	3.160	3.141
Ba–C22	3.071	3.100
Ba–C23	3.223	3.048
Ba–C24	3.249	3.300
Ba–C25	3.226	3.570
Ba–C26	3.077	3.441
Ba–N1	2.887	2.873
Ba–N2	2.882	2.924
Ba–N3	2.839	2.854
Ba–N4	2.942	2.864
Ba–X1A	2.936	2.870
Ba–X1B	2.940	3.069
Bond Angles		
X1A–Ba–X1B	112.3	116.4

ternal coordination of Ba^{2+} by solvent molecules.[4b,c] The X-ray structure presented here agrees with this analysis.

First obtained as an orange-yellow microcrystalline powder from the reaction of barium and fluorene in liquid ammonia at −80 °C,[5,6] 1 was dissolved in THF, from which

† In memoriam, Feb 21, 1964–Feb 16, 1992.

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