Reaction of the Ylide Complex [(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2P^+Ar_3$)]PF_6^- with n-Butyl-lithium–Tetramethylethylenediamine; Generation and Stereospecific Alkylation of a Transition Metal-substituted Wittig Reagent

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The title reaction (tetrahydrofuran, −24 °C, 2 h) gives [(η^5-C_5H_5)Re(NO)(PPh_3)($\bar{C}H$–P^+Ar_3)] (**2**; Ar = *p*-MeC_6H_4), which upon treatment with $MeOSO_2CF_3$ gives (*SS,RR*)-[(η^5-C_5H_5)Re(NO)(PPh_3){CH(Me)P^+Ar_3}]PF_6^- [(*SS,RR*)-(**3**)] stereospecifically.

The chemistry of co-ordinatively saturated phosphorus ylide complexes, $L_nMCH_2P^+R_3$, has been extensively studied.[1] Surprisingly, there have been few attempts to deprotonate ylide complexes to give transition metal-substituted ylides, or 'organometallic Wittig reagents' [*e.g.* equation (1)].[1—3] Subsequent alkylation would give a new chiral centre, and in the case of a chiral L_nM moiety might occur with appreciable 1,2-asymmetric induction. In view of current interest in metal-mediated asymmetric synthesis, we sought to determine if chiral rhenium ylide complexes could be converted into rhenium-substituted ylides and stereospecifically alkylated.

$$L_nM\text{-}CH_2P^+R_3 + B{:}^- \longrightarrow \{L_nM\text{-}\bar{C}H\text{-}P^+R_3 \longleftrightarrow L_nM\text{-}CH{=}PR_3\} + BH \quad (1)$$

The previously reported[4] ylide complex [(η^5-C_5H_5)-Re(NO)(PPh_3)($CH_2P^+Ph_3$)]PF_6^- did not give well defined reactions with Bu^nLi–TMEDA† in THF. We thought that this could be due to its poor THF solubility, so the more lipophilic complex [(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2P^+Ar_3$)] PF_6^- (**1**; Ar = *p*-MeC_6H_4) was synthesized from the methylidene complex[4] [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+PF_6^-$ and PAr_3 [^{31}P n.m.r. (p.p.m., $CDCl_3$) 40.11 (d, J_{PP} 17.9 Hz, PAr_3) and 20.82 (d, J_{PP} 17.8 Hz, PPh_3)].† Complex (**1**) and

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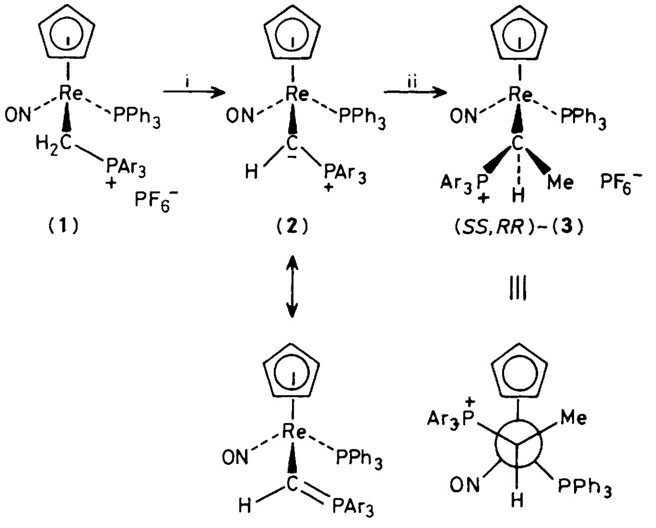
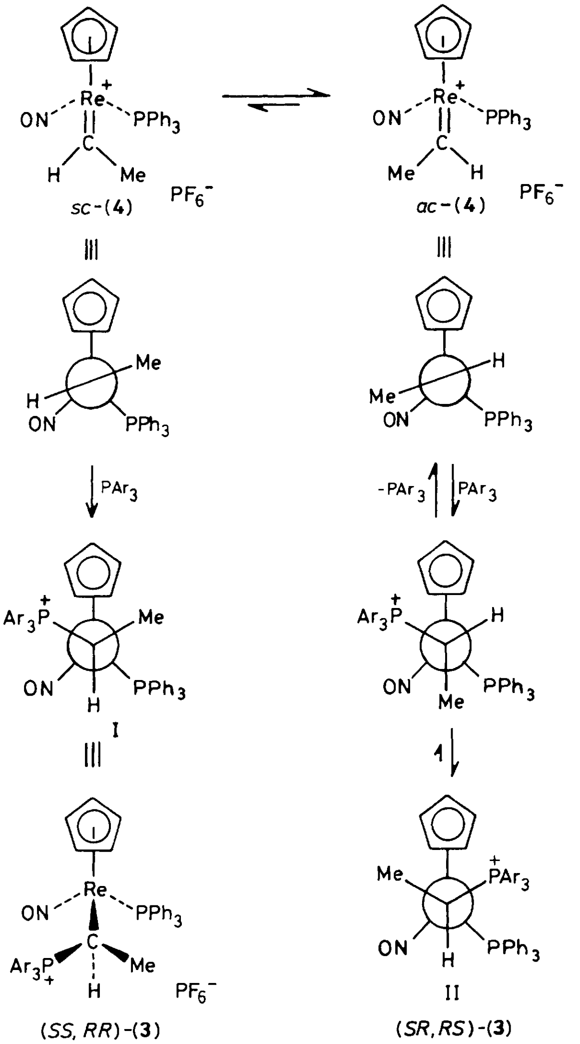
† TMEDA = tetramethylethylenediamine; THF = tetrahydrofuran. N.m.r., i.r., mass spectral, and microanalytical data for (**1**) and (*SS,RR*)-(**3**) (G. L. Crocco, Ph.D. Thesis, University of Utah, 1986) were furnished to the referees.



Scheme 1. Synthesis and stereospecific methylation of a rhenium-substituted ylide. Ar = *p*-MeC_6H_4. *Reagents:* i, Bu^{n}Li, TMEDA, −24 °C, 2 h; ii, $MeOSO_2CF_3$, −78 °C.

Bu^{n}Li–TMEDA reacted during 2 h at −24 °C in THF to give the ylide [(η^5-C_5H_5)Re(NO)(PPh_3)($\bar{C}H$–P^+Ar_3)] (**2**), as assayed by ^{31}P n.m.r. spectroscopy [30.27 (d, J_{PP} 22.7 Hz, PAr_3) and 15.21 (d, J_{PP} 22.4 Hz, PPh_3)] and subsequent methylation ($MeOSO_2CF_3$, −78 °C) to give the ylide complex (*SS*,*RR*)-[(η^5-C_5H_5)Re(NO)(PPh_3){CH(Me)P^+Ar_3}]PF_6^- [(*SS*,*RR*)-(**3**); Scheme 1]. Complex (*SS*,*RR*)-(**3**) was isolated in 83% yield after recrystallization.† Its gross structure followed from its spectroscopic properties [i.r. (cm^{-1}, KBr) $\nu_{N≡O}$ 1667s, ν_{P-F} 839s; ^{31}P n.m.r. (p.p.m., $CDCl_3$) 43.04 (d, J_{PP} 17.0 Hz, PAr_3) and 19.72 (d, J_{PP} 16.9 Hz, PPh_3); ^1H n.m.r. (δ, $CDCl_3$) 4.79 (s, C_5H_5), 3.64 (dq, J_{HH}, J_{HP} 7.0 Hz, ReCH), and 1.46 (dd, J_{HH} 7.0, J_{HP} 21.4 Hz, CH*Me*)],‡ and its stereochemistry was established by an independent synthesis (Scheme 2).

Authentic samples of (*SS*,*RR*)-(**3**), and the diastereoisomer (*SR*,*RS*)-(**3**), were prepared by PAr_3 attack upon the two Re=C geometric isomers of the ethylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=CHMe)]$^+PF_6^-$ (**4**).[5] It has been established that nucleophilic additions to this and related[6] alkylidene complexes occur preferentially from a direction *anti* to the bulky PPh_3 ligand, thus enabling rigorous assignments of product stereochemistry to be made. Reaction of PAr_3 with the *less* stable ethylidene Re=C isomer, *sc*-(**4**) (Scheme 2), gave (*SS*,*RR*)-(**3**) in quantitative spectroscopic yield (<10 min, −78 °C, CD_2Cl_2) and 90% isolated yield. Surprisingly, attempts to isolate (*SR*,*RS*)-(**3**) from the reaction of PAr_3 (2 equiv.) with the more stable ethylidene Re=C isomer, *ac*-(**4**), also gave (*SS*,*RR*)-(**3**). When this reaction was monitored by ^{31}P and ^1H n.m.r. spectroscopy in CD_2Cl_2 at −78 °C, rapid (<10 min) formation of a complex with plausible features for (*SR*,*RS*)-(**3**) was observed [^{31}P n.m.r. (p.p.m.) 39.29 (d, J_{PP} 15.8 Hz, PAr_3) and 21.63 (d, J_{PP} 16.3 Hz, PPh_3); ^1H n.m.r. (δ) 4.55 (s, C_5H_5), 3.46 (br. m, ReCH), and 1.52 (dd, J_{HH} 6.0, J_{HP} 21.6 Hz, CH*Me*)]. The reaction mixture was kept at room temperature for 2 days, after which time a (72 ± 2) : (28 ± 2) mixture of (*SS*,*RR*)-(**3**) and (*SR*,*RS*)-(**3**) was present. Hence, (*SR*,*RS*)-(**3**) is converted into the more stable (*SS*,*RR*)-(**3**), and would have been easily detected if present (≥1%) at any stage in the above syntheses of (*SS*,*RR*)-(**3**).



Scheme 2. Independent syntheses and equilibration of the two diastereoisomers of (**3**). Ar = *p*-MeC_6H_4.

Several aspects of the above results are noteworthy. First, we recently reported the deprotonation of the cyanomethyl complex [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CN)] to give the rhenium-substituted carbanion Li^+[(η^5-C_5H_5)Re(NO)(PPh_3)(:CHCN)]$^-$, and subsequent stereospecific methylation to give the cyanoethyl complex (*SR*,*RS*)-[(η^5-C_5H_5)Re(NO)(PPh_3){CH(Me)CN}].[7] Interestingly, the ylide (**2**) is methylated in an *opposite* stereochemical sense, indicating that the factors controlling alkylation stereospecificity are different for anionic and neutral Re–C_α nucleophiles. Secondly, (*SS*,*RR*)-(**3**) and (*SR*,*RS*)-(**3**) are the first Re–C_α diastereoisomers that we have observed to equilibrate. From recent data of Seeman, Davies,[8] Baird,[9] and ourselves,[10] it is believed that the bulkiest C_α substituent prefers to reside between the NO and η^5-C_5H_5 ligands, whereas the smallest C_α substituent prefers to reside between the NO and PPh_3 ligands (which subtend only a 90° angle). If the preferred Re–C_α rotamers of both diastereoisomers of (**3**) have H_α between the NO and PPh_3 ligands, then (*SR*,*RS*)-(**3**) will have a bulky PAr_3 substituent residing between the large PPh_3 and η^5-C_5H_5 ligands (II, Scheme 2), whereas

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‡ $^{13}C\{^1H\}$ N.m.r. data for (*SS*,*RR*)-(**3**) (δ, $CDCl_3$) 90.59 (s, C_5H_5), 23.54 (d, J_{CP} 1.7 Hz, CH*Me*), −12.75 (dd, J_{CP} 26.1, 1.9 Hz, ReCH). (*SR*,*RS*)-(**3**) is unstable except at −78 °C, so no ^{13}C n.m.r. analysis was attempted.

(*SS*,*RR*)-(**3**) will have a smaller Me substituent in the analogous location (I, Scheme 2). This accounts for the observed order of stability. We propose that this stability order will be general for diastereoisomeric $[(\eta^5\text{-}C_5H_5)M(L)(PPh_3)(CRR'R'')]$ complexes (L = NO or CO) with three sterically differentiated C_α substituents. Finally, Scheme 1 provides explicit precedent for previously proposed but unobservable C_α deprotonations of ylide complexes.[1—3]

We thank the N.I.H. for support of this research. N.m.r. spectrometers were provided by N.S.F. and D.O.D. instrument grants.

Received, 21st April 1986; Com. 535

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