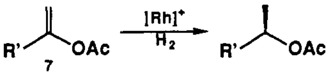
Table II. Asymmetric Hydrogenation of Enol Acetates **7**[a]

R′	ligand	previous best[b]	% ee,[c] confign[d]
C_6H_5	(*S*,*S*)-**2a**	64	89, (−)-*S*
p-$NO_2C_6H_4$	(*R*,*R*)-**1b**	65	90, (+)-*R*
m-ClC_6H_4	(*R*,*R*)-**2b**		91, (+)[e]
1-naphthyl	(*R*,*R*)-**1b**		94, (+)-*R*
1-naphthyl	(*S*,*S*)-**2a**		93, (−)-*S*
CO_2Et	(*S*,*S*)-**2a**	89	99, (−)-*S*
CO_2Et	(*R*,*R*)-**2b**	89	>99, (+)-*R*
CF_3	(*S*,*S*)-**2a**	77	94, (+)-*S*
CF_3	(*R*,*R*)-**1b**	77	>95, (−)-*R*

[a] Reaction conditions as in Table I. Reaction time for complete (100%) conversion was 2–12 h. [b] Values listed denote highest ee's previously reported for catalytic asymmetric hydrogenation of these substrates (see ref 8). [c] Enantiomeric excesses were determined as described in the supplementary material. [d] Product absolute configurations established by sign of optical rotations. [e] Absolute configuration not established.

these substrates (Table I). In addition, high catalytic rates and efficiencies (for methyl (*Z*)-α-acetamidocinnamate, S/C ratio = 10 000 with Et-DuPHOS) were demonstrated. Under the conditions described, methyl (*Z*)-α-benzamidocinnamate was hydrogenated to (*R*)-*N*-benzoylphenylalanine methyl ester in 98% ee and dimethyl itaconate was reduced to (*R*)-dimethyl 2-methylsuccinate in >95% ee with the Rh((*R*,*R*)-Et-DuPHOS) catalyst.

Substrate chelation through a secondary donor group (e.g., acetamido carbonyl oxygen) is thought to be crucial for the attainment of high enantiomeric excesses in many asymmetric hydrogenation reactions.[1,7] Efforts to identify other substrates which possess a similar grouping led us to examine the asymmetric hydrogenation of enol acetates **7** (Table II).[1c,8] These catalytic enol acetate hydrogenations are synthetically equivalent to asymmetric keto group reductions. Good to excellent enantioselectivities have been observed, and in comparison with the best results previously reported[8] for these substrates, much higher selectivities are noted here. In contrast to the acetamidoacrylates (**6**), no one ligand consistently outperformed the others in the hydrogenation of enol acetates. For a given substrate, the highest ee's were obtained through systematic "steric matching", which demonstrates the potential power of this approach in optimizing enantioselectivities.



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The presence of electron-withdrawing groups on an olefinic substrate is well-known to enhance late-transition-metal binding constants[9] and has been shown to result in higher rates and enantioselectivities in asymmetric hydrogenation reactions.[1,7] The high ee's we observe in hydrogenation reactions probably, in part, stem from the electron-rich nature of our phosphines, which increases electron density at the metal and leads to stronger olefin binding relative to most known asymmetric diphosphines which bear at least two aryl substituents on phosphorus.

The relative ease with which both antipodes of the new homochiral series of bis(phospholane) ligands **1** and **2** are prepared should lead to many applications in asymmetric catalysis; such studies are in progress.

Acknowledgment. The expert technical assistance of J. E. Feaster for synthetic work and J. Lazar for obtaining HRMS spectra and the invaluable advice obtained through insightful discussions with Drs. T. V. RajanBabu and W. A. Nugent (Du Pont CRD) are warmly acknowledged.

Supplementary Material Available: Experimental details including preparations and spectral and analytical data for phosphines **1** and **2**, cyclic sulfates **4**, and rhodium complexes **5** and enantiomeric excess determinations (17 pages). Ordering information is given on any current masthead page.

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Endohedral Complexes of Fullerene Radical Cations

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An interesting feature of the fullerenes[1] is the potential to confine atoms and atomic ions within their hollow center volume.[2-4] Such confinement of small species within larger cage molecules has been accomplished by synthesis in other areas of organic chemistry.[5]

One surprising method, however, of inserting the guest is by high-energy collisions of the C_{60} or C_{70} radical cations with helium target gas.[6] A series of even carbon number product ions[7] $C_n^{\bullet+}$ and $C_nHe^{\bullet+}$ (n = 48–58) were found, but the putative $C_{60}He^{\bullet+}$ precursor could not be seen. No other evidence for incorporation of other simple target gases (except ^3He) was reported,[6] although Ne uptake was mentioned in a note added in proof.[6]

We report the use of a new-design, four-sector tandem mass spectrometer[8] to expand the scope of fullerene endohedral complexes.[9] This instrument comprises two double-focusing mass spectrometers. The second stage, of reverse geometry design, possesses a planar rather than curved electrostatic analyzer (ESA),

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(7) We categorize product ions as all ions that are products of the collision of precursor ions with the target gas, including collisionally excited but undissociated molecular ions, all ions that contain the target gas, and fragment ions. Fragment ions are those ions produced from a well-defined precursor species as a result of the loss of neutral fragments.

(8) This instrument was commissioned by the Midwest Center for Mass Spectrometry, a former NSF regional instrumentation facility (Grant No. CHE 8620177). It was designed by Robert Bateman and built by VG Analytical (now Fisons Instruments) for the MCMS. Although the spectrometer has not been completely evaluated, it was briefly described by Gross: Gross, M. L. In *Methods in Enzymology, Mass Spectrometry*; McCloskey, J. A., Ed.; Academic Press: New York, 1990; Vol. 193, pp 131–153.

(9) The term endohedral, meaning "in the cage", originates from Cioslowski and Fleischmann: Cioslowski, J.; Fleischmann, E. D. *J. Chem. Phys.* **1991**, *94*, 3730.

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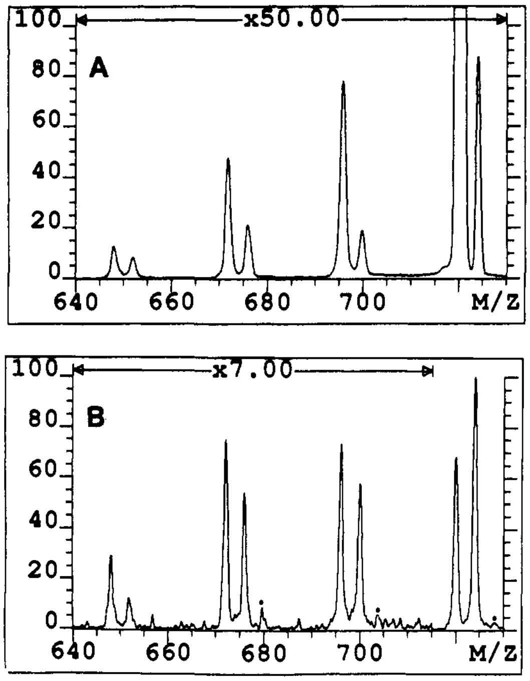

Figure 1. (A) Partial mass spectrum of product ions resulting from high-energy collisions (4-keV laboratory energy) of $C_{60}^{\bullet+}$ with He. The $C_{60}^{\bullet+}$ precursor ion beam is off scale. At this laboratory energy, the $C_{60}He^{\bullet+}$ product ion is more abundant than at 8-keV laboratory energy. (B) Partial spectrum of product ions from $C_{70}^{\bullet+}$ precursor ions (8 keV). The dots mark the $C_nHe_2^{\bullet+}$ series of ions, which is observed under conditions in which two or more collisions are expected to occur.

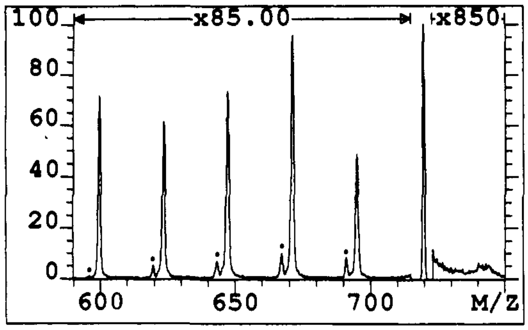

Figure 2. Partial mass spectrum of product ions resulting from high-energy (2-keV laboratory energy) collisions of $C_{60}^{\bullet+}$ with Ne. At this laboratory energy, the Ne-containing product ions, indicated with a dot, are more abundant than at 8-keV laboratory energy.

consisting of two widely spaced electrodes. This second stage is particularly suitable for studies of target gas capture because the ESA has a wide energy "bandpass". This is important because capture of the target gas will modify the kinetic energy of the product ion beams, as we[10] and others[12] have seen.

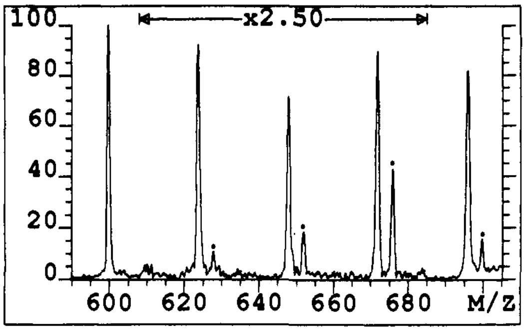

Figure 3. Partial mass spectrum of product ions resulting from high-energy (8-keV laboratory energy) collisions of $C_{60}^{\bullet+}$ with Ar. The dots mark the product ions resulting from capture of Ar.

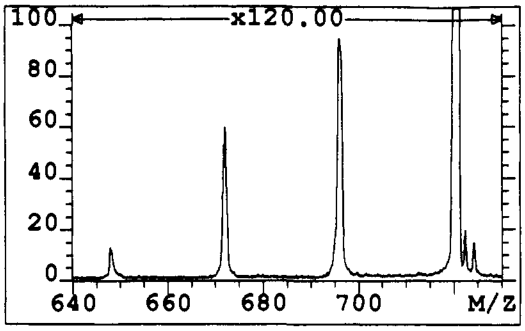

Figure 4. Partial mass spectrum of product ions resulting from high-energy (4-keV laboratory energy) collisions of $C_{60}^{\bullet+}$ with D_2. The two peaks at m/z 722 and 724 correspond to $C_{60}D^+$ and $C_{60}D_2^{\bullet+}$, respectively, and not to any ^{13}C-containing $C_{60}^{\bullet+}$ ions, which were removed by MS1.

High-energy collisions of helium and an 8-keV beam of C_{60} radical cations,[11] which was decelerated to 4 keV, produce a series of both $C_n^{\bullet+}$ and $C_nHe^{\bullet+}$ (see Figure 1A); the pattern is similar to that seen by Schwarz and co-workers.[6] But unlike in the previous work, we were able to detect the $C_{60}He^{\bullet+}$ product ion at m/z 724. Recently, Ross and Callahan[12] also detected $C_{60}He^{\bullet+}$ formed from $C_{60}^{\bullet+}$ by using a combined standard ESA and quadrupole as the detecting mass analyzer, and Schwarz and co-workers[6] observed $C_{60}He^{\bullet+}$ as a product from collisions of $C_{70}^{\bullet+}$ with He.

Collisions of 8-keV $C_{70}^{\bullet+}$ with He produce $C_{70}He^{\bullet+}$ (1% relative to $C_{70}^{\bullet+}$), which is more abundant than any of the other product ions. More significant is the production of a series of $C_nHe_2^{\bullet+}$ product ions, as well as a $C_nHe^{\bullet+}$ series (see Figure 1B). High-energy collisions of $C_{84}^{\bullet+}$ with He give rise to $C_{84}He^{\bullet+}$ (2% relative to $C_{84}^{\bullet+}$).

Neon is also captured by a $C_{60}^{\bullet+}$ beam that was selected after 8-kV acceleration and then decelerated to 2-keV energy. A series of product ions ranging possibly from $C_{44}Ne^{\bullet+}$ but unambiguously from $C_{46}Ne^{\bullet+}$ to $C_{56}Ne^{\bullet+}$ was detected[13] (a portion of the spectrum is given in Figure 2). Further, a broadened and weak signal appeared approximately where $C_{60}Ne^{\bullet+}$ is expected. The $C_{60}Ne^{\bullet+}$ is produced unambiguously from 8-keV collisions of $C_{70}^{\bullet+}$ with Ne.

Another interesting feature of the collisions of $C_{60}^{\bullet+}$ with He and Ne is the loss of a single carbon atom to give $C_{59}^{\bullet+}$ (ca. 1% of the $C_{58}^{\bullet+}$ abundance), which also can be seen in spectra in ref 6. This process cannot be substantiated by the data in Figure 2; 8-keV collisions are required.

Collisions (8-keV) with argon also cause incorporation of argon and decomposition to form a quite different series of product ions: $C_{55}Ar^{\bullet+}$, $C_{53}Ar^{\bullet+}$, $C_{51}Ar^{\bullet+}$, and $C_{49}Ar^{\bullet+}$, which are all *odd* carbon species (see Figure 3). An unresolved enigma has been, how do fullerene ions fragment (metastably,[14] by collisional activation,[15] and by photoactivation[16]) to eliminate only even carbon neutrals? Perhaps the odd carbon losses are promoted by the high center

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(10) Caldwell, K. A.; Giblin, D. E.; Gross, M. L., submitted to *J. Am. Chem. Soc.*

(11) The sample of C_{60}, which also contained C_{70} and C_{84}, was prepared by some of the authors and their colleagues at Exxon as previously described, except that helium was used as the moderating gas: Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, J.; Robbins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* **1991**, *113*, 2940.

(12) Ross, M. M.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 5720.

(13) The $C_{58}Ne^{\bullet+}$ is difficult to confirm because it overlaps with the low-mass skirt of the more intense $C_{60}^{\bullet+}$ signal.

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of mass collision energy (421 eV) for these $C_{60}^{\bullet+}$ collisions with argon.

Capture of simple molecular gases undergoing high-energy collisions with fullerene ions could not be documented previously.[6] For example, collisions of $C_{60}^{\bullet+}$ with D_2 gave rise to no D- or D_2-containing products.[6] We were able, however, to detect both $C_{60}D^+$ and $C_{60}D_2^{\bullet+}$ (see Figure 4). The inability to detect lower mass product ions containing D or D_2 in the experiments reported here and elsewhere[6] may be due to rupture of the D–D bond with subsequent loss of the deuteriums.

The results given here will be elaborated in a comprehensive report of the products and energetics of high-energy collisions of $C_{60}^{\bullet+}$, $C_{70}^{\bullet+}$, and other fullerene radical cations with a number of target gases.[10] Other issues addressed include the kinetic energy of product ions that contain the target gas, the variation of the spectra of product ions as a function of both energy and number of collisions, and the end points in the capture processes. Comparison of the predicted kinetic energies of product ions with the observed values convinces us that the majority of the fullerene product ions produced from high-energy collisions with small target gases result from fragmentation of the intermediate fullerene endohedral complex.[10]

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE 9017250). We acknowledge Robert Bateman of VG Analytical (Fisons Instruments), who designed the four-sector tandem mass spectrometer and provided advice on experimental aspects of this work.

3,3′,5,5′-Tetrapyridylbiphenyl: A Biscyclometalating Bridging Ligand with a High Coupling Ability in Ru^{III},Ru^{II} Mixed Valence Systems

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The search for bridging ligands allowing electronic communication between metal centers is an important target related to long-range electron transfer and photoinduced charge separation.[1] Following the pioneering work of Creutz and Taube on 1,4-pyrazine-bridged Ru^{II},Ru^{III} mixed valence complexes,[2] several bridging ligands of various lengths have been used.[3] Most of them and in particular 4,4′-bipyridine lead to class II complexes (valence-trapped systems).[4,5] Most coupling systems consist of short bridges insuring strong Π-communication like $(CN)_2$, N_2, $NCC^-(t\text{-Bu})CN$, or μ-η^2:η^2 benzene.[3,6,7] We now report that a bis-terdentate ligand containing two NCN coordination sites ("cyclometalating" terpyridine) affords dinuclear species in which the metals are connected by a 4,4′-biphenyl dianion (isoelectronic to the classical bridging ligand 4,4′-bipyridine), the whole edifice being stabilized by the four additional pyridine nuclei. The corresponding mixed-valence state (Ru^{III},Ru^{II}) can easily be generated. It shows exceptionally strong electronic interaction between the two redox centers.

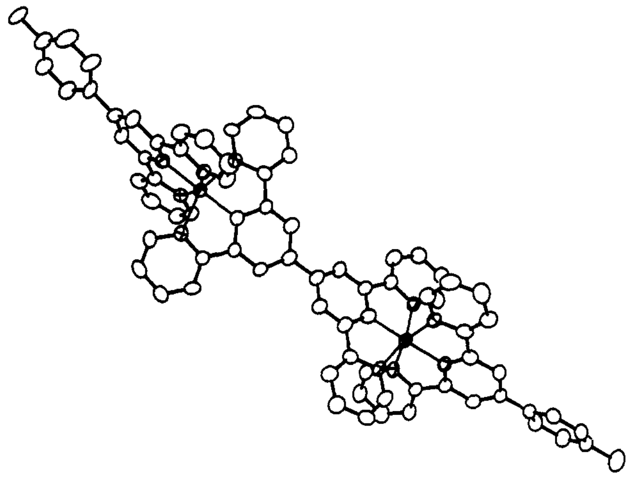
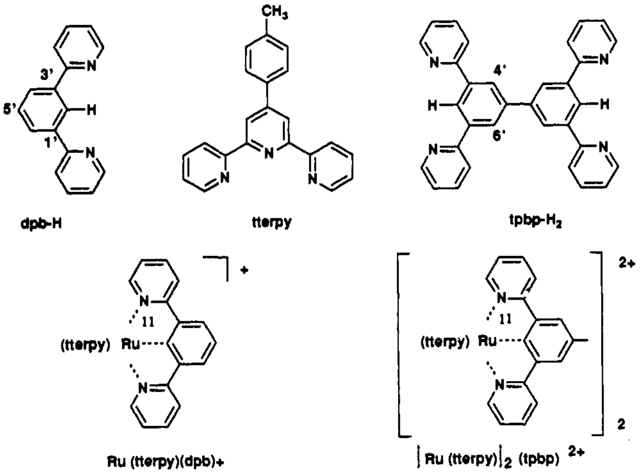


Figure 1. ORTEP drawing of the non-hydrogen atoms of the dinuclear complex cation. Thermal ellipsoids show 40% probability levels (empty ellipses, carbon). Main distances in angstroms: Ru1···Ru2, 11.009 (2); Ru-C, 1.96 (2) and 1.96 (1); Ru-N, 2.042 (8), 2.019 (8), 2.067 (9), 2.080 (8), 2.100 (8), 2.070 (8), 2.007 (7), 2.075 (8), 2.099 (8), and 2.089 (8). Torsion angle around the central C–C bond of the tpbp ligand, 22.2 (7)°.

Chart I



The compound studied and its precursors are represented in Chart I. The terdentate ligand dpb^- (dpb-H: di-(*o*-pyridyl-1,3-benzene) contains a σ-phenyl central coordination site. It was prepared[8] with the aim of using it as a terpy analogue displaying a stronger ligand field than terpy itself. $Ru(tterpy)(dpb)^+PF_6^-$ was prepared from $Ru(tterpy)Cl_3$ (tterpy: 4′-*p*-tolyl-2,2′,6′,2″-terpyridine) by first replacing the chloride ligands by solvent molecules using $AgBF_4$ in excess as a dechlorinating agent in refluxing acetone, followed by addition of a stoichiometric amount of dpb-H and heating of the mixture under reflux in 1-butanol. Depending upon the experimental conditions, various amounts of an additional dinuclear compound were obtained (up to 60% yield based on $Ru(tterpy)Cl_3$). The same dinuclear complex could be generated from $Ru(tterpy)(dpb)^+PF_6^-$ by reacting the mononuclear species with a large excess of silver(I) salt now used as an oxidant in refluxing butanol. The compound was obtained in 80% yield after chromatographic separation (silica; acetone–

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(8) dpb-H was prepared according to a synthetic method previously described for 2,2′-(1,4-phenylene)dipyridine.[9] 1,3-Dicyanobenzene (4 g; 32.2 mmol) and Co(Cp)COD (0.1 g; COD is 1,5-cyclooctadiene) dissolved in 40 mL of toluene were loaded in an autoclave under 10 atm of acetylene. The autoclave was heated to 130 °C for 3 days. After workup and chromatography (silica; CH_2Cl_2–CH_3OH as eluent), dpb-H was obtained as a colorless oil (6.5 g; 90%). ^1H NMR (200 MHz, CD_2Cl_2):δ 8.7 (m, 3 H), 8.09 (d, 2 H, 2 Hz), 8.06 (dd, 2 H, 2 Hz), 7.85 (m, 4 H), 7.58 (t, 1 H, 8 Hz), 7.27 (ddd, 2 H, 7, 4, 1.5 Hz). MS: $m/z = 232$; $C_{16}H_{12}N_2$ requires 232.

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