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[16] Crystals of **3b** were grown from cyclohexane/CHCl$_3$ ($C_{48}H_{26}N_4Ni$, M_w = 717.44). The selected crystal (dimensions: 0.32 × 0.14 × 0.10 mm) had an orthorhombic unit cell, space group $Pna2_1$, cell dimensions a = 7.3143(6), b = 21.296(2), c = 20.154(2) Å, V = 3139.2(4) Å^3, and Z = 4. Data were collected with ω-scans on a Bruker SMART 1000 diffractometer ($\lambda(\mathrm{Mo_{K\alpha}})$ = 0.71073 Å) at 90(2) K. A total of 40879 reflections were collected to $2\theta = 63°$. A 2θ cutoff of 55° was applied to afford 31351 total reflections: 7147 unique, 5573 observed ($I > 2\sigma$) (R_{int} = 0.109, $T_{\min}$ = 0.82, $T_{\max}$ = 0.94, ρ_{calcd} = 1.518 g cm^{-3}, μ = 0.665 mm^{-1}). An empirical absorption correction was applied (SADABS 2.0, G. M. Sheldrick, **2000**). The structure was solved by direct methods and refined based on F^2 using all data by full-matrix least-squares methods with 479 parameters (Bruker SHELXS-97, SHELXL-97). A Flack x parameter of 0.06(2) was determined. Hydrogen atom positions were refined with a riding model. Final R factors were $R1$ = 0.058 (observed data) and w$R2$ = 0.122 (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162682. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Olefin Metathesis with 1,1-Difluoroethylene**

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The recent development of ruthenium olefin-metathesis catalysts coordinated with N-heterocyclic carbene ligands is a significant advance because it extends the scope of the reaction to more challenging substrates, that is, those that are sterically hindered or that contain electronically deactivating groups, as well as monomers with low ring strain.[1–4] One set of substrates that has received relatively little attention, however, is the halogenated olefins;[5] the metathesis of allyl bromide, allyl chloride, and related substrates with the heterogeneous $Re_2O_7/Al_2O_3/Me_4Sn$ catalyst system are among the few examples.[6] Most recently, the cross metathesis of 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene with terminal olefin[4c] and the dimerization of vinyl *gem*-difluorocyclopropane derivatives[7] have been achieved using [(H$_2$IMes)(PCy$_3$)(Cl)$_2$Ru=CHPh] (**1**) (H$_2$IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; Cy = cyclohexyl). In these cases, the substrates are challenging because of the electron-withdrawing nature of the pendent halogens.

A particularly interesting situation arises when the olefin is directly halogenated, because then the metathesis reaction will involve a monohalo [M]=CXR or dihalo [M]=CX$_2$ carbene complex rather than the usual alkylidene [M]=CR$_2$. This possibility has been considered by Beauchamp and coworkers, who have speculated about the metathesis of directly fluorinated olefins with nickel or manganese complexes.[8] A tungsten dichlorocarbene complex [W]=CCl$_2$ has also been proposed as an active species in the W(CO)$_6$/CCl$_4$/$h\nu$ catalyst system.[9] To our knowledge, there has been only one report of metathesis involving directly halogenated olefins, namely the cross metathesis of 1-chloro- and 1-bromoethylene with propylene using $Re_2O_7/Al_2O_3/Me_4Sn$.[6e] Herein, we report the successful metathesis of 1,1-difluoroethylene with ruthenium catalyst **1**.

Under an atmosphere of 1,1-difluoroethylene, **1** reacts to form the corresponding methylidene [(H$_2$IMes)(PCy$_3$)(Cl)$_2$Ru=CH$_2$] (**2**)[10] and difluorocarbene [(H$_2$IMes)(PCy$_3$)(Cl)$_2$Ru=CF$_2$] (**3**) complexes [Eq. (1)].[11] When the reaction is performed at room temperature, the product mixture contains approximately 40 % methylidene (**2**) and 60 % difluorocarbene (**3**), as well as styrene and β,β-

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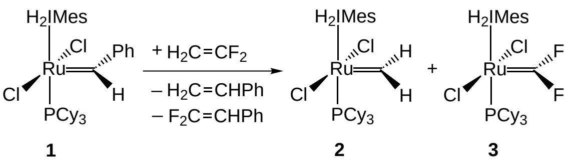

(1)

difluorostyrene. Remarkably, the amount of difluorocarbene complex formed increases to >98% when the reaction is carried out at 60°C. This difference suggests that pathway A of Figure 1 is preferred over pathway B at elevated temperatures. The organic products of a second turnover of olefin metathesis—ethylene and tetrafluoroethylene—were not observed in the product mixture, which indicates that the reaction is not catalytic. Nevertheless, the $H_2C{=}CF_2$ double bond is initially cleaved in a metathesis fashion, and as such, it is the first example of olefin metathesis involving a directly fluorinated olefin.

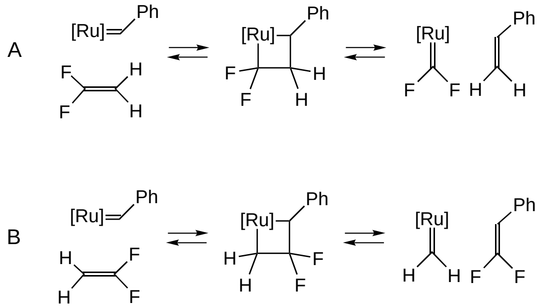

Figure 1. One turnover of olefin metathesis between the ruthenium benzylidene complex **1** and 1,1-difluoroethylene. Pathway A is favored at elevated temperatures.

Moreover, this transformation provides access to 16-electron ruthenium difluorocarbene complexes, which have not been previously accessible.[12] Complex **3** has been unambiguously identified as the difluorocarbene by NMR spectroscopy. It is characterized by a $^{31}P\{^1H\}$ NMR resonance signal at $\delta = 32.1$ and a ^{19}F NMR resonance at $\delta = 133.7$, both doublets with $J = 4.5$ Hz from $^{31}P-^{19}F$ coupling. This downfield ^{19}F chemical shift is also diagnostic for metal fluorocarbenes, which resonate between $\delta = 80$ and 200.[12, 13] The $^{13}C\{^1H\}$ resonance for the carbene carbon atom appears as a triplet of doublets at $\delta = 218.1$ ($^2J_{CP} = 12$ Hz, $^1J_{CF} = 432$ Hz). This resonance is shifted significantly upfield compared to those of related ruthenium alkylidenes; for example, the resonance signals of the benzylidene carbon of **1** and the methylidene carbon of **2** appear at $\delta = 295.1$ and 294.8, respectively.[14]

The molecular structures of **2** and **3** were determined by X-ray diffraction (Figures 2 and 3). Notably, complex **2** is the first structurally characterized ruthenium methylidene (Figure 2). In both cases, the carbene is oriented in the [Cl-Ru-Cl] plane.[15] The d(Ru=C) of 1.800(2) Å in **2** is shorter than that typical for ruthenium benzylidene complexes ([Ru]=CHPh) but similar to values observed for phenyl-substituted vinylidenes ([Ru]=C=CHPh).[16]

Complex **3** (Figure 3), which is isostructural with **2**, exhibits an even shorter Ru=C bond length of 1.775(3) Å.[17] This value is also short compared to the d(Ru=C) of 1.83(1) Å for $[(PPh_3)_2(CO)_2Ru{=}CF_2]$, a trigonal bipyramidal, 18-electron complex reported by Roper and co-workers.[15a, 18] This difference between $[(PPh_3)_2(CO)_2Ru{=}CF_2]$ and **3** may be rationalized by enhanced π back bonding from the more electron-rich metal center of **3** to the carbene carbon atom.

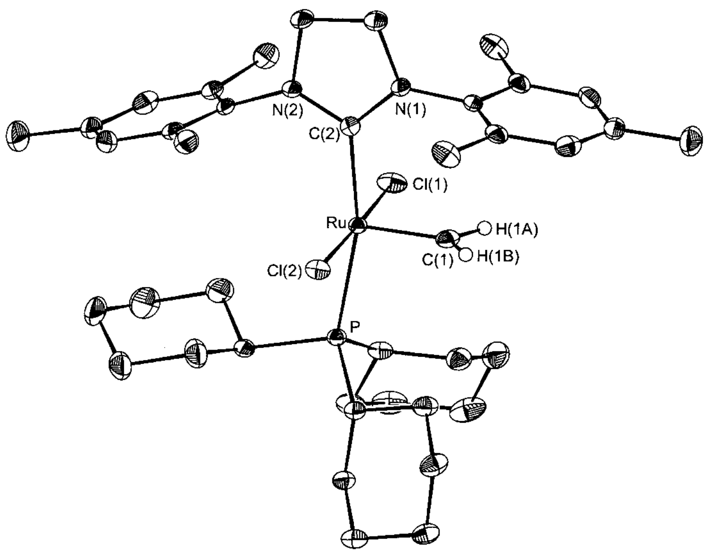

Figure 2. Molecular structure of **2**. For clarity, all hydrogen atoms except H(1A) and H(1B) have been omitted. Thermal ellipsoids are set at 50% probability; H(1A) and H(1B) are drawn at arbitrary scale. Selected bond lenghts [Å] and angles [°]: Ru-C(1) 1.800(2), Ru-C(2) 2.065(2), Ru-Cl(1) 2.379(1), Ru-Cl(2) 2.393(1), Ru-P 2.427(1); Cl(1)-Ru-Cl(2) 177.05(2), C(2)-Ru-P 165.81(5), H(1A)-C(1)-H(1B) 108(2).

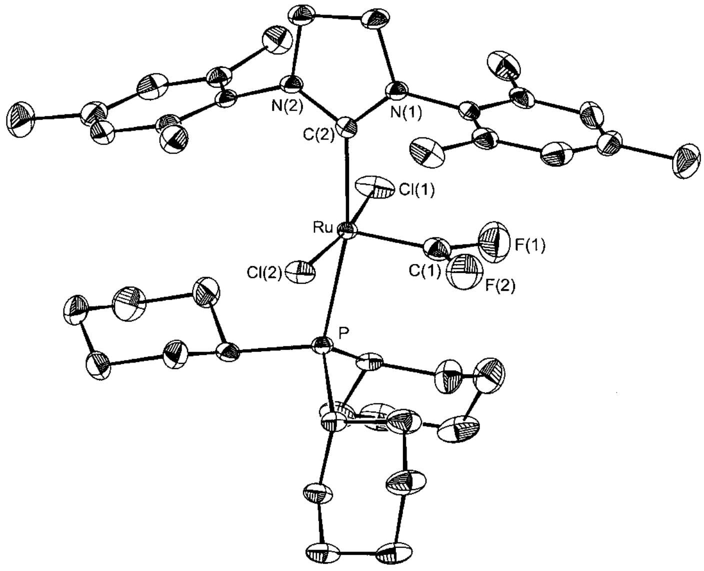

Figure 3. Molecular structure of **3**. For clarity, all hydrogen atoms have been omitted. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Ru-C(1) 1.775(3), Ru-C(2) 2.076(2), Ru-Cl(1) 2.365(1), Ru-Cl(2) 2.385(1), Ru-P 2.433(1), F(1)-C(1) 1.335(3), F(2)-C(1) 1.305(3); Cl(1)-Ru-Cl(2) 170.90(3), C(2)-Ru-P 167.69(6), F(2)-C(1)-F(1) 103.4(2).

We are also interested in the olefin metathesis activity of **3** itself. The results in Table 1 provide a measure of the activities of **1**–**3** for the ring-opening metathesis polymerization (ROMP) of cycloocta-1,5-diene (COD).[3c, 4d, 14] Compared to

Table 1. ROMP of COD with catalysts **1**–**3**.[a]

Catalyst	T [°C]	Additive[b]	t [h]	Product[c] [%]
1[d]	20	–	0.03	100
2[d]	20	–	1.25	62
3	25	–	1.25	9
3	50	–	5	72
3	50	CuCl	5	81
3	50	HCl	5	92
3	50	$AlCl_3$	5	21

[a] Conditions: 0.005 M [catalyst] and 300 equivalents COD in CD_2Cl_2. [b] 5 equivalents of additive; HCl used as a 1 M solution in Et_2O. [c] Percent conversion determined by ^1H NMR integration. [d] Ref. [14].

the superior activity of **1**, complex **3** is a poor catalyst. We suspected that the problem was catalyst initiation because no NMR signals for CF_2 end groups in the polymer were visible. Recent studies have shown that the rate-limiting step for the initiation of $[(L)(PR_3)(X)_2Ru{=}CHR']$ catalysts is phosphane dissociation.[14, 19] For **3**, $^{31}P\{^1H\}$ NMR magnetization-transfer experiments revealed no detectable phosphane dissociation up to 100 °C ($k < 0.01\ s^{-1}$).[20, 21]

Higher temperatures and additives that promote phosphane dissociation helped improve the activity of **3** (Table 1).[22] The best results were obtained with HCl, which is capable of reversible phosphane protonation. In contrast, addition of $AlCl_3$ resulted in an immediate and irreversible decomposition reaction.

The reaction of 1,1-difluoroethylene with ruthenium catalyst **1** is significant for several reasons. Most importantly and of general interest, it demonstrates that olefin metathesis with directly fluorinated substrates is possible. Encouraged by these results, ongoing work is directed toward the application of olefin metathesis as a mild and selective method for the synthesis of halogenated molecules. Of greater interest to the organometallic chemist, this reaction provides a new method for the synthesis of electronically unsaturated halocarbene complexes. In addition, the structural data for a matched pair of ruthenium carbene complexes will aid our understanding of the bonding in this important catalyst family.

Experimental Section

Synthesis of **3**: A solution of **1** (0.32 g 0.37 mmol) in dry, degassed benzene (15 mL) in a thick-walled glass ampule was put under ~1.5 atm of 1,1-difluoroethylene. The mixture was heated at 60 °C for 12 h, during which time it changed from reddish to brown. The solution was then concentrated to 5 mL and purified by column chromatography in air (silica gel, 5:1 pentane:THF). The orange fraction was stripped of solvent and dried under vacuum: yield 0.26 g (86 %). ^1H NMR (499.852 MHz, 25 °C, CD_2Cl_2): $\delta = 1.118$ (br, 15 H, PCy_3), 1.626 (br, 15 H, PCy_3), 2.248 (s, 3 H, *p*-CH_3 of Mes), 2.285 (s, 3 H, *p*-CH_3 of Mes), 2.385 (m, 3 H, PCy_3), 2.480 (s, 6 H, *o*-CH_3 of Mes), 2.551 (s, 6 H, *o*-CH_3 of Mes), 4.003 (s, 4 H, NCH_2CH_2N), 6.921 (s, 4 H, *m*-H of Mes); $^{13}C\{^1H\}$ NMR (125.705 MHz, 30 °C, C_6D_6): $\delta = 19.44$ (s, CH_3 of Mes), 20.65 (s, CH_3 of Mes), 21.49 (s, CH_3 of Mes), 21.50 (s, CH_3 of Mes), 26.92 (d, $J = 1.3$ Hz, PCy_3), 28.50 (d, $J = 10$ Hz, PCy_3), 30.14 (s, PCy_3), 33.34 (d, $J = 18$ Hz, PCy_3), 51.86 (d, $^4J_{PC} = 2.6$ Hz, NCH_2CH_2N), 52.61 (d, $^4J_{PC} = 3.5$ Hz, NCH_2CH_2N), 127.30 (s, Mes), 128.17 (s, Mes), 129.26 (s, Mes), 129.51 (s, Mes), 130.11 (s, Mes), 130.52 (s, Mes), 134.68 (d, $^4J_{PC} = 0.7$ Hz, *ipso*-C of Mes), 136.85 (s, *ipso*-C of Mes), 138.91 (s, Mes), 138.93 (s, Mes), 139.03 (s, Mes), 139.67 (s, Mes), 217.23 (d, $^2J_{CP} = 87$ Hz, NCN), 218.09 (td, $^2J_{CP} = 12$ Hz, $^1J_{CF} = 430$ Hz, $Ru{=}CF_2$); ^{19}F NMR (282.192 MHz, 25 °C, CD_2Cl_2): $\delta = 133.74$ (d, $^3J_{FP} = 4.5$ Hz); $^{31}P\{^1H\}$ NMR (121.392 MHz, 25 °C, CD_2Cl_2): $\delta = 32.15$ (t, $^3J_{PF} = 4.4$ Hz); IR (KBr pellet): $\tilde{\nu} = 1167$ and 1172 cm^{-1} (ν_{C-F}).

Crystal structure of **2**: The complex was synthesized by the method in ref. [14]. Orange-brown crystals were obtained by slow evaporation of a concentrated hexanes solution. $C_{40}H_{61}Cl_2N_2Ru$, $M_w = 772.85$, monoclinic, $a = 12.2168(6)$, $b = 18.0193(8)$, $c = 18.1162(9)$ Å, $\beta = 103.651(1)°$, $V = 3875.4(3)$ Å^3, $\rho_{calcd} = 1.325\ Mg\,m^{-3}$, $T = 98$ K, space group $P2_1/n$ (No. 14), $Z = 4$, radiation $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $\mu = 0.613\ mm^{-1}$, $\theta_{max} = 28.46°$, 56743 reflections measured, 9201 unique ($R_{int} = 0.0542$), structure solved by direct methods, refinement of F^2 against all reflections using SHELXL-97,[23] 659 parameters, 0 restraints, final $R_1 = 0.0414$, $wR_2 = 0.0555$ (all data), $GOF = 1.645$, max/min residual density $+0.666/-0.476\ e\,Å^{-3}$.

Crystal structure of **3**: Orange crystals were obtained by slow evaporation of a concentrated hexanes solution. $C_{40}H_{59}Cl_2F_2N_2Ru$, $M_w = 808.83$, monoclinic, $a = 12.2295(6)$, $b = 18.4137(9)$, $c = 18.1269(9)$ Å, $\beta = 103.709(1)°$, $V = 3965.7(3)$ Å^3, $\rho_{calcd} = 1.355\ Mg\,m^{-3}$, $T = 98$ K, space group $P2_1/n$ (No. 14), $Z = 4$, radiation $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $\mu = 0.610\ mm^{-1}$, $\theta_{max} = 28.41°$, 58469 reflections measured, 9430 unique ($R_{int} = 0.0575$), structure solved by direct methods, refinement of F^2 against all reflections using SHELXL-97,[23] 668 parameters, 0 restraints, final $R_1 = 0.0528$, $wR_2 = 0.0693$ (all data), $GOF = 1.899$, max/min residual density $+0.953/-0.636\ e\,Å^{-3}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162849 (for **2**) and -162850 (for **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Structure factors are available on request from xray@caltech.edu.

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[16] The average *d*(Ru=C) for the seven ruthenium benzylidene complexes in the Cambridge Structural Database is 1.85 Å. The average *d*(Ru=C) for the 20 phenyl-substituted ruthenium vinylidene complexes is 1.80 Å. CSD Version 5.20. *3D Search and Research Using the Cambridge Structural Database*, F. H. Allen, O. Kennard, *Chemical Design and Automation News* **1993**, *8*, p. 1 and pp. 31–37.

[17] Interestingly, in the other matched pair of methylidene and dihalocarbene complexes, the metal–carbene bond lengths *increase* in going from the methylidene [(PPh$_3$)$_2$(NO)(Cl)Os=CH$_2$] (1.92(1) Å) to the difluorocarbene [(PPh$_3$)$_2$(NO)(Cl)Os=CF$_2$] (1.976(6) Å). a) A. F. Hill, W. R. Roper, J. M. Waters, A. H. Wright, *J. Am. Chem. Soc.* **1983**, *105*, 5939; b) M. A. Gallop, W. R. Roper, *Adv. Organomet. Chem.* **1986**, *25*, 121.

[18] Another structurally characterized ruthenium difluorocarbenne complex is [(P*i*Pr$_3$)$_2$(CO)(F)(H)Ru=CF$_2$], which contains an even longer *d*(Ru=C) of 1.952(3) Å. In this case, however, the hydride ligand is located *trans* to the difluorocarbene, see ref. [13].

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[20] The phosphane dissociation rate for **1** is 1.64 s^{-1} at the same temperature. See refs. [14] and [19].

[21] Notably, complex **3** is stable at this temperature. In contrast, **2** decomposes at elevated temperatures, even in the presence of free PCy$_3$. As a result, it has not been possible to measure the phosphane dissociation rate for **2**. See ref. [14].

[22] a) J. P. Morgan, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 3153; b) M. S. Sanford, L. M. Henling, R. H. Grubbs, *Organometallics* **1998**, *17*, 5384; c) E. L. Dias, R. H. Grubbs, *Organometallics* **1998**, *17*, 2758; d) D. M. Lynn, B. Mohr, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 1627.

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A Unique Asymmetric [Mn$_3^{II}$] Triple-Stranded Helicate from a Symmetric Pentadentate Ligand[**]

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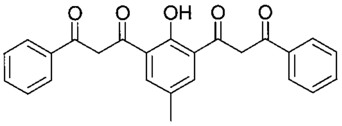
One of the richest parcels of supramolecular chemistry is that where the various components of a complex assembly recognize and associate with each other "via" the intermediacy of coordination bonds.[1] In this area, the specific coordination requirements of transition metals are combined with the electronic and structural features of new ligands in the design and construction of unprecedented molecular architectures displaying novel and exciting properties. This approach has been relatively unexplored in the field of molecular magnetism.[2] We have recently started a program aimed at the design and preparation of novel multidentate ligands as a means of assembling transition metal centers into species displaying new topologies and innovative magnetic properties. In this context, we have built in the same molecule two β-diketone units and a phenol group to produce a symmetric O-pentadentate ligand (H$_3$L).[3] The preparation of some related molecules and their use as dinucleating ligands have been reported in the literature.[4] We intended to use a basic form of H$_3$L as a template to bring in proximity a number of transition metals in discrete, molecular arrays. Examples of such systems involving oligo-α-pyridylamine ligands are known.[2e, 5] We now report the first case with an oxygen donor ligand and introduce an unprecedented asymmetric topology within the context of coordination helicates.



Reaction of H$_3$L with one equivalent of Mn(AcO)$_2\cdot$4H$_2$O in the solvent mixture MeOH/py (2/1, v/v) leads to a yellow crude product upon precipitation with hexanes. Recrystallization of this product from CH$_2$Cl$_2$/Et$_2$O/hexanes affords yellow needles of [Mn$_3$(HL)$_3$] (**1**) in an overall yield of 15%. The structure of **1**[6] (Figure 1) consists of a trinuclear array of Mn^{II} ions chelated and bridged by three HL^{2-} ligands wrapped around the molecular axis in an irregular helical

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