(58%), 720 (65%), 719 (100%), 718 (99%), 716 (60%), 457 (70%), 456 (69%), 455 (82%), 262 (18%).

Equilibration Studies. All equilibrium values were determined in $CDCl_3$ at room temperature (20 °C) in a septum-sealed NMR tube by integration of the respective ^{31}P signals in the NMR spectrum after 24 h of reaction (when no further changes were observed in the NMR spectrum). Equilibrium constants were determined for both the forward and reverse reactions and calculated from the known values of the concentrations of the starting complex and the respective ligands.

Equilibration of 6 and 5 (Eq 9). Complex **6** (17.4 mg, 1.76×10^{-2} mmol) was dissolved in 0.450 mL of $CDCl_3$ solution containing 0.176 mmol of CH_3CN. After equilibration and integration of the ^{31}P signals K was calculated to be 4.2×10^{-3}. For the reverse reaction 17.5 mg (1.84×10^{-2} mmol) of **5** was dissolved in a mixture of 0.250 mL of $CDCl_3$ containing 3.14×10^{-2} mmol of pyridine and 0.360 mL of $CDCl_3$ containing 8.10×10^{-2} mmol of CH_3CN. After equilibration and integration of the respective ^{31}P signals K was found to be 4.0×10^{-3} for an average value of $K = (4.1 \pm 0.1) \times 10^{-3}$.

Equilibration of 3a and 5 (Eq 10). The equilibrium constant for the forward reaction was found to be 0.225 by dissolving 21.9 mg (1.87×10^{-2} mmol) of **3a** in 0.350 mL of $CDCl_3$ containing 7.88 mmol of CH_3CN. For the reverse reaction K was found to be 0.146 by dissolving 25.6 mg (2.69×10^{-2} mmol) of **5** and 13.0 mg (4.96×10^{-2} mmol) of Ph_3P in $CDCl_3$.

Equilibration of 6 and 3a (Eq 11). The value of K was found to be 0.035 from 12.1 mg (1.22×10^{-2} mmol) of **6** and 6.6 mg (2.52×10^{-2} mmol) of Ph_3P in $CDCl_3$. For the reverse reaction K was found to be 0.0175 by dissolving 21.1 mg (1.80×10^{-2} mmol) of **3a** and 1.36 mmol of pyridine in $CDCl_3$ for an average value of $K = (2.6 \pm 0.9) \times 10^{-2}$.

Equilibration of 6 and 4 (Eq 12). CO was bubbled through 0.740 mL of a $CDCl_3$ solution of 18.0 mg (1.82×10^{-2} mmol) of **6** for 1 h in an NMR tube, which was then sealed with a septum. Integration of the ^{31}P signals gave a K value of 1.49×10^{-2}. For the reverse reaction 27.1 mg (2.89×10^{-2} mmol) of **4** and 5.64×10^{-2} mmol of pyridine were dissolved in 0.778 mL of $CDCl_3$ in an NMR tube, which was flushed with CO for 0.5 h and then sealed under CO with a septum. Integration of the ^{31}P signals gave a K value of 0.940×10^{-2} for an average $K = (1.2 \pm 0.3) \times 10^{-2}$.

Acknowledgment. Financial support by the NSF (Grant No. CHE8802622) and the generous loan of K_2PtCl_4 by Johnson Matthey are gratefully acknowledged.

Supplementary Material Available: Tables of all bond distances and angles, positional parameters, least-squares planes, and displacement parameter for **9b** (14 page); a listing of observed and calculated structure factors for **9b** (14 pages). Ordering information is given any any current masthead page.

Nickel, Palladium, and Platinum Complexes Derived from Octafluorocyclooctatetraene. Synthesis of 1-2:5-6-η-Octafluorocyclooctatetraene Complexes of Nickel(0) and η²-Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl Complexes of Nickel(II), Palladium(II), and Platinum(II)

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The zerovalent complexes $[M(COD)_2]$ (M = Pt, Ni; COD = 1,5-cyclooctadiene) and $[Ni_2(COT)_2]$ (COT = 1,3,5,7-cyclooctatetraene) do not react with octafluorocyclooctatetraene (**1**). Addition of 2 equiv of a ligand to $[Pt(COD)_2]$, followed by **1**, affords the octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes **7** (L = PPh_3, $AsPh_3$, *t*-BuNC). In two cases, octafluorocycloocta-2,5,7-triene-1,4-diyl intermediates **8** (L = PPh_3, $AsPh_3$) were observed by ^{19}F NMR spectroscopic monitoring of the reaction mixture. The tetrakis(phosphine) complexes $[ML_4]$ also react with **1** to afford octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes **7** (M = Pt; L = PPh_2Me, $PPhMe_2$) and **10** (M = Pd; L = PPh_3). The palladium analogue **10** (L = *t*-BuNC) has also been prepared by addition of *t*-BuNC to tris(dibenzylideneacetone)dipalladium, followed by addition of **1**. In contrast, reaction of **1** with $[Ni(COD)L_2]$, prepared in situ from $[Ni(COD)_2]$ and 2 equiv of L, yields the four-coordinate 1-2:5-6η-OFCOT complexes **11** (L = PMe_3, $PPhMe_2$), which do not react further to give octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes of Ni(II). Addition of other ligands (L = PCy_3, PPh_3, PPh_2Me, $P(OPh)_3$, $P(OMe)_3$) to solutions of $[Ni(COD)_2]$ and **1** result in no reaction with OFCOT. Similary the complexes $[Ni(C_2H_4)L_2]$ (L = PPh_3, PPh_2Me) do not react with **1**. In contrast, addition of 2 equiv of *t*-BuNC to $[Ni(COD)_2]$ in the presence of **1** yields the four-coordinate octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complex **12**. This latter compound does not exchange the *t*-BuNC ligands with exogenous ligands, nor does it undergo any reductive elimination chemistry but instead forms the five-coordinate adducts **13** (L = PMe_3, PPh_3, *t*-BuNC). Comparisons are made of the chemistry of **1** with group 10 metals and the previously reported chemistry of cobalt and rhodium.

Introduction

Octafluorocyclooctatetraene (OFCOT, **1**)[1,2] possesses a varied transition-metal coordination chemistry, which in many respects differs significantly from that of its hydrocarbon analogue cyclooctatetraene (COT).[3] We have previously shown that photolysis of the (pentamethylcyclopentadienyl)cobalt and -rhodium complexes **2a,b**

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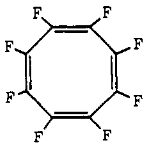
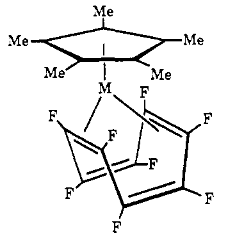
[1] Lemal, D. M.; Buzby, J. M.; Barefoot, A. C., III; Grayston, M. W.; Laganis, E. D. *J. Org. Chem.* **1980**, *45*, 3118–3120.

[2] Laird, B. B.; Davis, R. E. *Acta Crystallogr. Sect. B.* **1982**, *B38*, 678–680.

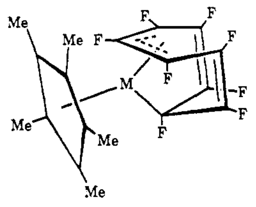
[3] For reviews of the organic and organometallic chemistry of cyclooctatetraene see: (a) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University Press: Cambridge, U.K., 1978. (b) Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: New York, 1979.



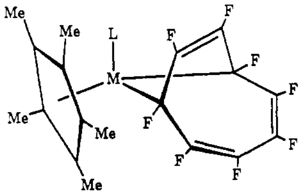
1



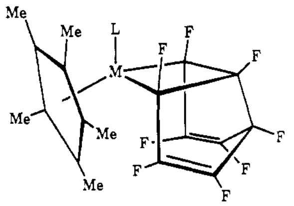
2 a. M = Co
b. M = Rh



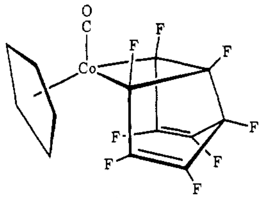
3 a. M = Co
b. M = Rh



4 a. M = Co; L = t-BuNC
b. M = Rh; L = t-BuNC
c. M = Rh; L = PMe$_3$



5 a. M = Co; L = t-BuNC
b. M = Rh; L = t-BuNC



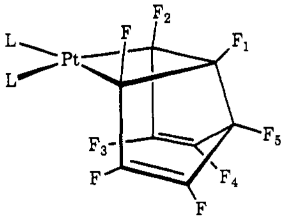
6

yields a photostationary mixture of starting materials and their 1-3:6-η-OFCOT ligation isomers **3a,b**, in which a formal intramolecular oxidative addition of OFCOT to the metal center has occurred.[4] While the 1-2:5-6-η isomers **2** are thermally unreactive toward exogenous ligands, their 1-2:5-6-η isomers **3** do react further with *tert*-butyl isocyanide (*t*-BuNC) to afford initially the spectroscopically characterized octafluorocycloocta-2,5,7-triene-1,4-diyl complexes **4a,b** via a ligand-promoted η^3 to η^1 rearrangement of the fluorinated ligand.[4] These diyl intermediates then undergo a thermal transannular ring closure reaction to afford the octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl isomers **5a,b**.[4] A stable rhodium diyl complex was isolated with use of trimethylphosphine as the added ligand and was shown crystallographically to possess structure **4c**.[5] The cobalt complex **6**, containing an octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl ligand analogous to those in complexes **4**, has also been crystallographically characterized.[6]

Here we report reactions of Ni(0), Pd(0), and Pt(0) complexes with OFCOT which give chemistry similar to that reported for the cobalt and rhodium systems discussed above. The mode of ligation of OFCOT to the metal is shown to depend upon the metal and the ancillary ligands, and in some cases transannular ring closure is shown to occur spontaneously in the absence of exogenous ligands. Parts of this work have appeared as preliminary communications,[6-8] in one of which some structures of intermediates and products were assigned incorrectly.[7]

Results and Discussion

Platinum Chemistry of OFCOT. A useful starting material for the organometallic chemistry of platinum is bis(1,5-cyclooctadiene)platinum(0), [Pt(COD)$_2$], from which the cyclooctadiene moieties can be displaced easily by a variety of other ligands.[9] Reaction of [Pt(COD)$_2$] itself with OFCOT did not produce any metal–fluorocarbon products after 2 h, as evidenced by ^{19}F NMR spectroscopy. However, the addition of 2 molar equiv of triphenylphosphine to a solution of [Pt(COD)$_2$] in hexane followed by addition of OFCOT yielded **7a**, whose structure was confirmed by comparison of its ^{19}F NMR spectra with those of the crystallographically characterized cobalt complex **6**[6] and its relatives **5**.[4] Assignments of ^{19}F NMR resonances for **7a** were made by similar spectral comparisons. Similarly, reactions of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] or [PtL$_4$] (L = PPh$_3$, PPh$_2$Me, PMe$_2$Ph) with OFCOT led eventually to the 16-electron ring-closed products **7a–c**. Notably the absence of a symmetry plane that includes the Pt–P bonds is indicated by the observation of two ^{1}H NMR resonances due to diastereotopic methyl groups in the PMe$_2$Ph ligands of **7c**. The structures of **7a–c** were erroneously assigned as 1-3:6-η-OFCOT complexes in a preliminary communication.[7]



7 a. L = PPh$_3$
b. L = PPh$_2$Me
c. L = PPhMe$_2$
d. L = AsPh$_3$
e. L = t-BuNC

Evidence for a single intermediate in some of these reactions could be obtained spectroscopically, but the intermediates were not isolated. They subsequently disappeared with concomitant formation of the final transannular ring closed products **7**. For example, monitoring the reaction of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] with OFCOT in an NMR tube indicated the presence of an intermediate that exhibited four resonances of equal intensity in the ^{19}F NMR spectrum (shifts upfield from CFCl$_3$: δ 115.6, 139.1, 160.2, 186.4). The resonance at δ 139.1, which is assigned to the fluorines attached to the coordinated carbons, shows strong coupling to platinum ($J_{\text{Pt-F}}$ = 256 Hz). Comparison of the ^{19}F NMR spectrum of this intermediate species with that of **4c** indicates that the bonding of the C$_8$F$_8$ ring to the metal is the same in both species, and accordingly we assign structure **8a** to this intermediate. The structure of

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(4) Carl, R. T.; Hughes, R. P.; Samkoff, D. E. *Organometallics* **1988**, *7*, 1625–1631.

(5) Hughes, R. P.; Carl, R. T.; Hemond, R. C.; Samkoff, D. E.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 306–308.

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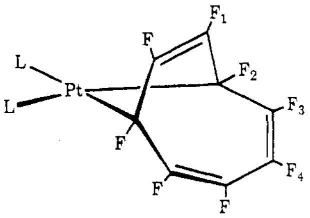
(7) Barefoot, A. C., III; Corcoran, E. W., Jr.; Hughes, R. P.; Lemal, D. M.; Saunders, W. D.; Laird, B. B.; Davis, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 970–972.

(8) Hughes, R. P.; Carl, R. T.; Samkoff, D. E.; Davis, R. E.; Holland, K. D. *Organometallics* **1986**, *5*, 1053–1055.

(9) (a) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 3–4. (b) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271–277. (c) Spencer, J. L. *Inorg. Synth.* **1979**, *19*, 213–218.

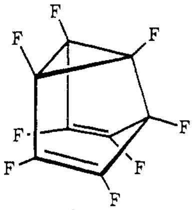


8 a. L = PPh_3
b. L = $AsPh_3$

this and the related intermediates were erroneously assigned as 1-2-η-OFCOT complexes in a preliminary communication.[7] Intermediate **8a** converted cleanly to **7a** after standing in solution overnight.

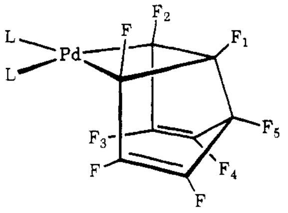
Likewise, reaction of $[Pt(COD)_2]$ with 2 equiv of triphenylarsine followed by addition of OFCOT yielded the analogous intermediate **8b**, which eventually afforded the ring-closed product **7d**. Formation of the ring-closed product **7e** also occurred when *tert*-butyl isocyanide was used as the added ligand. This reaction afforded **7e** more rapidly, and no intermediate species were observed in the ^{19}F NMR spectrum.

It was hoped that reductive elimination of the fluorocarbon ligand from **7** might afford the elusive valence isomer of OFCOT, perfluorosemibullvalene (**9**). Attempts to induce formation of **9** by initial oxidative addition of methyl iodide to **7**, followed by reductive elimination of the fluorocarbon from a Pt(IV) intermediate, led only to OFCOT as evidenced by ^{19}F NMR spectroscopy. Attempts to form perfluorosemibullvalene under mild conditions from other organic precursors have also failed, suggesting that it is a fragile molecule with respect to isomerization to OFCOT.[10] Thus, we cannot distinguish whether reductive elimination occurs to give perfluorosemibullvalene, which then rapidly ring-opens, or whether OFCOT is formed directly by a retrotransannular reaction during displacement from the metal under these conditions.



9

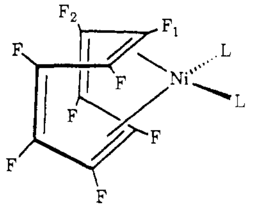
Palladium Chemistry of OFCOT. Since $[Pd(COD)_2]$ is difficult to synthesize and thermally unstable,[11] more convenient palladium(0) starting materials were used. The reaction of tris(dibenzylideneacetone)dipalladium[12] with 2 equiv of *tert*-butyl isocyanide per Pd atom, followed by addition of OFCOT, led to the analogous ring-closed product **10a**. Isolation of this complex was hampered by the presence of free dibenzylideneacetone and product decomposition upon room-temperature column chromatography on silica gel. However, elution of the reaction residue with methylene chloride on ethyl acetate deactivated silica gel at −55 °C yielded pure **10a**, which was characterized by its ^{19}F NMR spectrum and by microanalysis. A similar reaction of $[Pd(PPh_3)_4]$ with OFCOT afforded the phosphine analogue **10b**. No attempts were made to probe any further chemistry of these molecules.



10 a. L = t-BuNC
b. L = PPh_3

Nickel Chemistry of OFCOT. Four-Coordinate $[NiL_2(C_8F_8)]$ Complexes. Reaction of $[Ni(COD)_2]$ with OFCOT led to decomposition of the nickel starting material as evidenced by the formation of a nickel mirror on the side of the reaction flask. ^{19}F NMR spectroscopy indicated that no metal–fluorocarbon products were formed. Similarly, reaction of $[Ni_2(COT)_2]$ with OFCOT yielded no metal–fluorocarbon products as evidenced by ^{19}F NMR spectroscopy.

However, reaction of $[Ni(COD)_2]$ with 2 equiv of trimethylphosphine, followed by addition of OFCOT, led to formation of the complex **11a**, in which the OFCOT ring is bound to the metal center in a manner previously unseen in the group 10 triad. The ring is coordinated to the metal in the 1-2:5-6-η mode as evidenced by two resonances of equal intensity in the ^{19}F NMR spectrum. The resonance at δ 155.7 can be assigned to the fluorines attached to the coordinated carbons (F_1), and the resonance at δ 118.1 can be assigned to the fluorines attached to the uncoordinated carbons (F_2) on the basis of a comparison of the ^{19}F NMR chemical shifts with those of the analogous complexes **2**.[4] The analogous 1-2:5-6-η-OFCOT complex **11b** was also produced with use of dimethylphenylphosphine as the added ligand. In contrast to that for the Pt complex **7c**, the ^1H NMR spectrum of **11b** exhibits only a single methyl resonance for the PMe_2Ph ligands, indicating the presence of a symmetry plane which includes the Ni–P bonds. Attempts to isomerize the C_8F_8 ring in compounds **11a**,**b** via heating or ultraviolet irradiation led only to the recovery of starting materials. In reactions using PMe_3 or $PPhMe_2$ it is important that the phosphine be coordinated to the metal before OFCOT is added, since the free phosphine reacts with OFCOT to afford PR_3F_2 and other uncharacterized fluorine-containing materials.[13]



11 a. L = PMe_3
b. L = $PPhMe_2$

Attempts to make the corresponding diphenylmethylphosphine, triphenylphosphine, tricyclohexylphosphine, triphenyl phosphite, and trimethyl phosphite derivatives from $[Ni(COD)_2]$ were unsuccessful. Similarly, attempts to produce fluorocarbon complexes from the thermal reaction of $[Ni(C_2H_4)(PPh_3)_2]$ or $[Ni(C_2H_4)(PPh_2Me)_2]$ with OFCOT gave no observable reaction.

In contrast to these results, when $[Ni(COD)_2]$ was treated with 2 molar equiv of *tert*-butyl isocyanide, followed by OFCOT, the complex **12** was isolated, in which the OFCOT ring had isomerized to the ring-closed form.

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(10) Lemal, D. M. Unpublished observations communicated to R.P.H.

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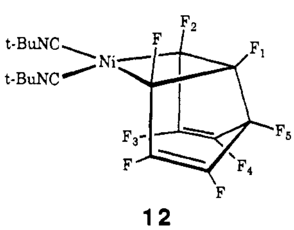
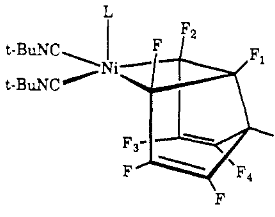


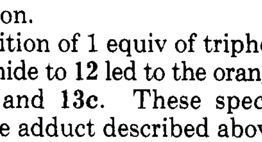
12



13 a. L = PMe_3
b. L = PPh_3
c. L = t-BuNC

Five-Coordinate [Ni(t-BuNC)$_2$L(C_8F_8)] Complexes. We were intrigued as to whether replacement of the *tert*-butyl isocyanide ligands in 12 with trimethylphosphine would lead to ligand substitution with retention of the ring-closed structure or whether substitution by phosphines would cause ring opening to give the 1-2:5-6-η complex **11a**. To our surprise, neither result was obtained. Addition of excess trimethylphosphine to a solution of 12 caused an immediate color change from orange to cherry red. The ^{19}F NMR spectrum of the resultant crystalline product **13a** exhibited five resonances of relative intensity 1:2:2:2:1. Comparison of the ^{19}F NMR chemical shifts and coupling constants of this complex with those of 12 indicated that the C_8F_8 ring was still bound to the metal center in the ring-closed form, although, at low temperatures, the chemical shifts of the resonance due to F_2 (the fluorines attached to the coordinated carbon atoms) was shifted upfield by 16 ppm when compared to the corresponding resonance in 12. The ^1H NMR spectrum of **13a** exhibited resonances at δ 0.90 (s, 18 H) and 1.10 (d, 9 H), indicating the retention of both *tert*-butyl isocyanide ligands and addition of one trimethylphosphine ligand to the coordination sphere. An X-ray diffraction study of **13a** has confirmed the five-coordinate structure in the solid state,[8] in which the complex adopts an approximate square-pyramidal geometry about the nickel center with PMe_3 in the apical position.

Similarly, addition of 1 equiv of triphenylphosphine or *tert*-butyl isocyanide to 12 led to the orange five-coordinate complexes **13b** and **13c**. These species and the trimethylphosphine adduct described above are rare examples of stable five-coordinate *cis*-dialkyl complexes of Ni(II), although stable trigonal-bipyramidal *trans*-dialkyls of nickel are well-known.[14] We have previously noted that these complexes provide a structural model for a putative square-pyramidal intermediate in reductive-elimination reactions of *cis*-dialkylnickel(II) complexes.[8] However, these fluorocarbon complexes **13a–c** are considerably more stable than the five-coordinate tris(triphenylphosphine)-nickelacyclopentane complex 14, which decomposes above 9 °C in solution.[15]



14

The apical phosphine ligands in **13a** and **13b** appear to dissociate reversibly in solution at room temperature as evidenced by the temperature-dependent chemical shifts of the α-fluorines (F_2) of the fluorinated metallacycle. However, the basal *tert*-butyl isocyanide ligands do not undergo ligand substitution at room temperature, even in the presence of excess phosphine. Assuming that ligand dissociation occurs from the apical site, we conclude that there is no energetically accessible pathway for interconversion of basal and apical sites which would allow dissociation of the t-BuNC ligands and their subsequent replacement by phosphine. A Berry pseudorotation is perhaps unlikely since the metallacyclobutane ring would have to span basal/apical sites, and a turnstile rotation of the three monodentate ligands is also precluded by these observations. However, only a single proton resonance for the *tert*-butyl isocyanide ligands was observed for the (t-BuNC)$_3$ complex **13c**, even at −80 °C, so we cannot exclude the possibility of rapid turnstile or Berry pseudorotation in this particular complex.

Conclusions. The transannular ring closure reaction seen in the organometallic chemistry of OFCOT has no precedent in the chemistry of its hydrocabon analogue COT.[3] It seems clear that a key intermediate which precedes transannular ring closure is a 1–4-η-octafluorocycloocta-2,5,7-triene-1,4-diyl complex,[4] a ligation mode which also has no precedent in the organometallic chemistry of COT.[3] We have previously proposed a pathway by which this intermediate might be transformed to the final octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl ligand[4] and have attributed some thermodynamic driving force for this overall reaction to the fact that electronegative fluorine prefers to be bound to carbon orbitals rich in p character.[16] The transannular closure allows four fluorinated carbons to change from formal sp^2 (in OFCOT) to sp^3 hybridization, provided that the combination of metal and ancillary ligands can support the required increase in the formal oxidation state and the appropriate coordination requirements of the metal center.[4]

In previously reported Co and Rh chemistry, access to the diyl intermediates 4, and hence the ring-closed products 5, occurs via exogenous ligand-induced η^3 to η^1 rearrangement of the 1-3:6-η-OFCOT complexes 3.[4] No spectroscopic evidence for analogous 1-3:6-η-OFCOT coordination has been obtained in any of the Ni, Pd, or Pt systems reported here, although their presence among other unobserved intermediates en route to the spectroscopically observed diyl intermediates 8 cannot be discounted. In the platinum chemistry reported here, ancillary ligands with varying steric and electronic effects, such as phosphines, triphenylarsine, and t-BuNC, all give rise to a transannular ring-closure reaction. Notably, however, [Pt(COD)$_2$] itself is unreactive, perhaps because the metal center is less basic. We conclude that in all cases the Pt(0) fragment "PtL$_2$" is electron rich enough to be capable of an oxidative-addition reaction with OFCOT to afford a 16-electron square-planar Pt(II)–diyl intermediate (e.g. 8) rather than a 1-3:6-η-OFCOT complex. Thus, in contrast to Co(III) and Rh(III) complexes 3, in which 1-3:6-η-OFCOT ligation is required to maintain the 18-electron pseudooctahedral coordination geometry around the metal, Pt(II) prefers the 16-electron square-planar structure, which can accommodate the 1–4-η-diyl ligand and allows subsequent ring closure to occur spontaneously without requiring an exogenous ligand. A similar argument can be made for the two palladium systems examined.

In contrast, the nickel chemistry of OFCOT is much more dependent on the nature of the ancillary ligand. Less basic phosphines (PPh_3, PPh_2Me) and phosphites (P(OPh)$_3$, P(OMe)$_3$) and the sterically demanding phosphine

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PCy_3 result in no observable binding of OFCOT, whereas more basic phosphines ($PPhMe_2$, PMe_3) with smaller cone angles result in binding of OFCOT without any oxidative addition. We conclude that the ability of "NiL_2" to bind OFCOT appears to be controlled by both the steric requirements of the phosphine and the basicity of the metal center. We also note that, in contrast to the 1-2:5-6-η-OFCOT complexes **2**, their Ni(0) analogues **11** do not undergo a photochemical (or thermal) rearrangement to 1-3:6-η-OFCOT isomers, and consequently no subsequent ring closure has been observed. Of all the ligands examined, only *t*-BuNC affords a ring-closed product containing square-planar Ni(II).

Experimental Procedures

General Considerations. Infrared spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer. ^1H NMR spectra (300 MHz), $^{31}P\{^1H\}$ NMR spectra (121.4 MHz), and $^{13}C\{^1H\}$ spectra (75 MHz) were recorded on a Varian Associates XL-300 spectrometer at 25 °C unless otherwise noted. ^{19}F NMR spectra were recorded on a JEOL FX60Q spectrometer (56.20 MHz) or on a Varian Associates XL-300 spectrometer (282 MHz) at 25 °C unless otherwise noted. All ^{19}F chemical shifts were referenced with positive shifts in ppm upfield from the internal standard of $CFCl_3$. All ^1H and $^{13}C\{^1H\}$ chemical shifts were referenced in ppm downfield from tetramethylsilane. Chemical shifts for $^{31}P\{^1H\}$ spectra were referenced in parts per million upfield relative to 85% H_3PO_4 by measuring the $^{31}P\{^1H\}$ spectrum of $P(OMe)_3$ under identical conditions and taking the chemical shift of $P(OMe)_3$ to be +141.0 ppm.[17] All variable-temperature NMR spectra were taken on a Varian Associates XL-300 spectrometer. The probe was calibrated at various temperatures by using samples of methanol (low temperature)[18] and ethylene glycol (high temperature).[19]

Melting points were determined by using an Electrothermal capillary melting point apparatus and are uncorrected. Positive ion fast atom bombardment (FAB) mass spectra were recorded at the Johns Hopkins School of Medicine Middle Atlantic Mass Spectrometry Laboratory. Microanalyses were done at Spang Microanalytical Laboratory, Eagle Harbor, MI.

All solvents were dinitrogen saturated and distilled over a variety of drying agents: benzene and tetrahydrofuran over potassium, toluene over sodium, hexane and diethyl ether over sodium–potassium alloy, and methylene chloride over P_4O_{10}. Reactions were run in oven-dried glassware with use of conventional Schlenk techniques, under an atmosphere of dinitrogen that were deoxygenated over BASF catalyst and dried with Aquasorb, or in a Vacuum Atmospheres drybox equipped with a HE-492 gas purification system. Column chromatography was done under dinitrogen in jacketed columns with dry, N_2-saturated chromatography supports and solvents. All deuterated solvents were dried over P_4O_{10} and degassed prior to use. Photolyses were performed with use of the borosilicate glass filtered output of a Hanovia 450-W Hg arc lamp unless otherwise noted.

Potassium tetrachloroplatinate(II) and palladium(II) chloride were obtained from Matthey Bishop, Inc. 1,5-Cyclooctadiene was obtained from Aldrich Chemical Co. and distilled from sodium prior to use. Triphenylphosphine, triphenylphosphite, and trimethylphosphite were obtained from Aldrich Chemical Co. and used as supplied. *tert*-Butyl isocyanide, dimethylphenylphosphine, diphenylmethylphosphine, and tricyclohexylphosphine were obtained from Strem Chemical Co. Trimethylphosphine (PMe_3) was prepared by a modification of the procedure of Wolfsberger and Schmidbaur.[20] Octafluorocyclooctatetraene (OFCOT **1**) was prepared according to the method of Lemal.[1] Bis(1,5-cyclooctadiene)platinum(0), $[Pt(COD)_2]$,[9c] tetrakis(phosphine) complexes $[PtL_4]$ (L = PPh_2Me, $PPhMe_2$)[21] and $[Pd(PPh_3)_4]$,[21] tris(dibenzylideneacetone)dipalladium–trichloromethane, $[Pd_2(DBA)_3]\cdot CHCl_3$,[12] bis(triphenylphosphine)(η-ethylene)nickel(0),[22] and bis(diphenylmethylphosphine)(η-ethylene)nickel(0)[22] were prepared according to literature methods. Bis(1,5-cyclooctadiene)nickel(0), $[Ni(COD)_2]$, was prepared according to the method of Schunn and stored at −20 °C under N_2 with aluminum foil as a cover.[23] $[Ni_2(COT)_2]$ was prepared by using the literature procedure.[24]

Attempted Reaction of Bis(1,5-cyclooctadiene)platinum(0) with OFCOT. A solution of $[Pt(COD)_2]$ (0.02 g, 0.049 mmol) in C_6D_6 (0.4 mL) was placed in a dry 5 mm NMR tube and OFCOT (0.012 g, 0.049 mmol) was added. The mixture was monitored by ^{19}F NMR spectroscopy, which only exhibited the single resonance due to unreacted OFCOT after 24 h.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(triphenylphosphine)platinum(II) (7a). Synthetic-Scale Reaction. $[Pt(COD)_2]$ 0.20 g, 0.5 mmol) was dissolved in dry hexane (25 mL). To this solution was added triphenylphosphine (0.26 g, 1.0 mmol) in dry hexane (25 mL) via a dropping funnel. The solution turned immediately from pale yellow to a bright orange color with the formation of an orange crystalline solid. Addition of OFCOT (0.124 g, 0.5 mmol) caused the precipitate to redissolve. After the mixture was stirred overnight, the solvent was removed under reduced pressure and the residue was crystallized from methylene chloride/hexane at −20 °C to give a white crystalline solid (0.36 g, 75%). **7a**: mp 223 °C dec; IR (KBr) $\nu_{C=C}$ 1710, 1720 cm^{-1}; ^{19}F NMR (acetone-d_6; see text for numbering): δ 135.4 (m, F_3), 141.3 (m, F_1), 159.1 (m, F_4), 185.9 (m, F_2), 193.3 (m, F_5), $J_{1,4} = 15$, $J_{1,5} = 15$, $J_{4,5} = 17$, $J_{1,2} = 4$, $J_{2,3} = 27$, $J_{Pt-F1} = 350$, $J_{Pt-F4} = 50$, $J_{Pt-F3} = 69$, $J_{Pt-F2} = 233$, $J_{P-F2} = 7$, $J_{P-F3} = 9$, $J_{P-F1} = 9$ Hz. Anal. Calcd for $C_{44}H_{30}F_8P_2Pt$: C, 54.61; H, 3.13; F, 15.71. Found: C, 54.61; H, 3.31; F, 15.55.

NMR Tube Reaction. $[Pt(COD)_2]$ (0.042 g, 0.098 mmol), OFCOT (0.024 g, 0.098 mmol), and triphenylphosphine (0.064 g, 0.244 mmol) were dissolved in $CDCl_3$ (1.0 mL), and the solution was placed in a 5-mm NMR tube. When the reaction was monitored with use of ^{19}F NMR spectroscopy, the intermediate **8a** was observed, which appeared after 10 min and exhibited four resonances in the ^{19}F NMR spectrum (δ 115.6 (F_1), 139.1 (F_2, $J_{Pt-F} = 256$ Hz), 160.2 (F_3), 186.5 (F_4); see text for numbering). After it stood overnight, the solution only exhibited ^{19}F NMR resonances due to the ring-closed product **7a**.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(methyldiphenylphosphine)platinum(II) (7b). OFCOT (0.25 g, 1 mmol) was added to a solution of $[Pt(PPh_2Me)_4]$ (0.5 g, 0.5 mmol) in benzene (10 mL), and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the oily residue was crystallized from Et_2O–hexane at −20 °C to afford **7b** as white crystals (0.36 g, 85%). **7b**: mp 188 °C dec; ^{19}F NMR (benzene-d_6) δ 137.4 (d, F_3), 140.2 (m, F_1), 157.7 (m, F_4), 182.6 (m, F_2), 193.1 (m, F_5) (the coupling patterns for the fluorines are approximately the same as for the triphenylphosphine complex **7a** described above); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −2.5 ($J_{Pt-P} = 2220$ Hz); ^1H NMR ($CDCl_3$) δ 1.80 (PMe, $J_{P-H} = 9$, $J_{Pt-H} = 24$ Hz), 7.35 (m, PPh); MS *m/e* 843 (M^+). Anal. Calcd for $C_{34}H_{26}F_8P_2Pt$: C, 48.41; H, 3.11. Found: C, 48.55; H, 3.33.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(dimethylphenylphosphine)platinum(II) (7c). OFCOT (0.75 g, 3 mmol) was added to a solution of $[Pt(PPhMe_2)_4]$ (1.20 g, 1.6 mmol) in benzene (20 mL), and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the oily residue was crystallized from Et_2O–hexane at −20 °C to afford **7c** as pale yellow crystals (0.80 g, 69%). **7c**: mp 108 °C dec; ^{19}F NMR ($CDCl_3$), δ 137.5 (m, F_3), 140.5 (m, F_1), 157.8 (m, F_4) 182.8 (m, F_2), 192.0 (m, F_5) (the coupling patterns for the fluorines are approximately the same as for the triphenylphosphine complex **7a** described above); ^1H NMR ($CDCl_3$) δ 1.55 (PMe, $J_{P-H} = 9$, $J_{Pt-H} = 26$ Hz), 1.49 (PMe, $J_{P-H} = 9$, $J_{Pt-H} = 26$ Hz), 7.35 (m, PPh). Anal. Calcd for $C_{24}H_{22}F_8P_2Pt$: C, 40.05;

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H, 3.06. Found: C, 40.35; H, 3.30.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(triphenylarsine)platinum(II) (7d). Synthetic-Scale Reaction. Triphenylarsine (0.306 g, 1.0 mmol) and OFCOT (0.124 g, 0.5 mmol) were dissolved in dry benzene (5 mL). [Pt(COD)$_2$] (0.20 g, 0.5 mmol) was added as a solid in small portions. A white solid precipitated. Addition of methylene chloride (8 mL) caused the solid to redissolve. The solvent was removed under reduced pressure, and the residue was crystallized from methylene chloride–hexane at −20 °C to give a white, crystalline solid (0.40 g, 76%). **7d**: mp 196–197 °C; IR (CH$_2$Cl$_2$) $\nu_{C=C}$ = 1722, 1705 cm^{-1}; ^{19}F NMR (acetone-d_6) δ 137.10 (q, F$_3$), 142.33 (m, F$_1$), 158.04 (m, F$_4$), 178.54 (m, F$_2$), 192.61 (m, F$_5$), $J_{1,2}$ = 15, $J_{1,5}$ = 15, $J_{2,3}$ = 27, $J_{2,5}$ = 4, $J_{4,5}$ = 17, $J_{\text{Pt-F5}}$ = 10, $J_{\text{Pt-F2}}$ = 270, $J_{\text{Pt-F3}}$ = 62, $J_{\text{Pt-F4}}$ = 80, $J_{\text{Pt-F1}}$ = 430 Hz; MS *m/e* 1055 (M$^+$). Anal. Calcd for $C_{44}H_{30}As_2F_8Pt$: C, 50.04; H, 2.86. Found: C, 49.90; H, 2.90.

NMR Tube Reaction. [Pt(COD)$_2$] (0.04 g, 0.098 mmol), OFCOT (0.024 g, 0.098 mmol), and triphenylarsine (0.057 g, 0.186 mmol) were dissolved in benzene-d_6 (1.0 mL), and the solution was placed in a 5-mm NMR tube. When the reaction was monitored with use of ^{19}F NMR spectroscopy, the intermediate **8b** was observed. This intermediate exhibited four resonances in the ^{19}F NMR spectrum (δ 114.0, 137.8, 158.1, 117.7). After it stood overnight, the solution only exhibited ^{19}F NMR resonances due to the ring-closed product **7d**.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(*tert*-butyl isocyanide)platinum(II) (7e). *tert*-Butyl isocyanide (0.125 mL, 1.16 mmol) and OFCOT (0.124 g, 0.5 mmol) were dissolved in dry benzene (10 mL). [Pt(COD)$_2$] (0.20 g, 0.5 mmol) was added as a solid in small portions. The color of the solution changed from bright red to gold. The solvent was removed under reduced pressure, and the ^{19}F NMR spectrum of the residue indicated quantitative formation of **7e**. Recrystallization of this residue several times from methylene chloride–hexane at −20 °C was required to give an analytically pure, white crystalline solid (0.079 g, 26%). **7e**: mp 157–158 °C; IR (CH$_2$Cl$_2$) $\nu_{N\equiv C}$ = 2223, 2200, $\nu_{C=C}$ = 1724, 1708 cm^{-1}; ^{19}F NMR (C$_6$D$_6$) δ 142.83 (m, F$_3$, F$_1$), 158.13 (m, F$_4$), 190.63 (m, F$_2$), 194.44 (m, F$_5$) (the coupling patterns for the fluorines are approximately the same as for the triphenylarsine complex **7d** described above); MS *m/e* 609 (M$^+$); Anal. Calcd for $C_{18}H_{18}F_8N_2Pt$: C, 35.47; H, 2.98; N, 4.60. Found: C, 35.52; H, 3.02; N, 4.56.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(*tert*-butyl isocyanide)palladium(II) (10a). [Pd$_2$(DBA)$_3$]·CHCl$_3$ (0.517 g, 0.5 mmol) was dissolved in THF (20 mL). To this deep purple solution was added *tert*-butyl isocyanide (0.228 mL, 2.0 mmol) via a gastight syringe. An immediate color change to green was observed. OFCOT (0.248 g, 1.0 mmol) was added as a solid. The reaction mixture was stirred for 8 h, and then the solvent was removed under reduced pressure. Low-temperature column chromatography (−55 °C) under N$_2$ on ethyl acetate deactivated silica gel was performed on the residue. Elution with methylene chloride (30 mL) afforded a tan solid upon removal of the solvent under reduced pressure. Elution with diethyl ether (50 mL) gave a yellow band, which proved to be DBA by IR and ^{1}H NMR spectroscopy. The tan solid was crystallized from diethyl ether–hexane to give pinkish needlelike crystals (0.096 g, 18%). **10a**: mp 123–125 °C; IR (C$_6$D$_6$) $\nu_{N\equiv C}$ = 2200, 2190, $\nu_{C=C}$ = 1713, 1703 cm^{-1}; ^{19}F NMR (C$_6$D$_6$) 133.43 (m, F$_1$), 142.16 (m, F$_3$), 159.17 (m, F$_4$), 197.09 (m, F$_2$, F$_5$) (the coupling patterns for the fluorines are approximately the same as for the triphenylarsine complex **7d** described above (without the platinum couplings)); MS *m/e* 520 (M$^+$). Anal. Calcd for $C_{18}H_{18}F_8N_2Pd$: C, 41.52; H, 3.48; N, 5.38. Found: C, 41.47; H, 3.53; N, 5.32.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(triphenylphosphine)palladium(II) (10b). OFCOT (0.215 g, 0.9 mmol) was added to a solution of [Pd(PPh$_3$)$_4$] (0.5 g, 0.45 mmol) in benzene (10 mL), and the mixture was stirred overnight. The solvent was removed under reduced pressure, and the residue was crystallized from Et$_2$O at −20 °C to afford the product as pale yellow crystals (0.15 g, 80%): mp 109–112 °C dec; ^{19}F NMR (CDCl$_3$) δ 135.30 (d, F$_3$), 132.40 (m, F$_1$), 159.47 (m, F$_4$), 192.89 (m, F$_2$), 194.53 (m, F$_5$). Anal. Calcd for $C_{44}H_{30}F_8P_2Pd$: C, 60.12; H, 3.44. Found: C, 60.44; H, 3.56.

Attempted Reaction of Bis(1,5-cyclooctadiene)nickel(0) with OFCOT. OFCOT (0.60 g, 2.27 mmol) was added to a stirred solution of [Ni(COD)$_2$] (0.275 g, 1.0 mmol) in benzene (10 mL). The solution was stirred for 4 days, at which time a nickel mirror had appeared on the side of the reaction flask. A ^{19}F NMR spectrum of the solution revealed only the single resonance of unreacted OFCOT.

Attempted Reaction of [Ni$_2$(COT)$_2$] with OFCOT. To a stirred solution of [Ni$_2$(COT)$_2$] (0.275 g, 1.0 mmol) in benzene (10 mL) was added OFCOT (0.30 g, 2.27 mmol). The solution was stirred in the dark for 7 days. A ^{19}F NMR spectrum of the solution revealed only the single resonance of unreacted OFCOT.

(1-2:5-6-η-Octafluorocyclooctatetraene)bis(trimethylphosphine)nickel(0) (11a). To a stirred yellow solution of [Ni(COD)$_2$] (0.38 g, 1.4 mmol) in THF (15 mL) was added PMe$_3$ (0.28 mL, 2.8 mmol) via a gastight syringe. After 1 h, OFCOT (0.35 g, 1.4 mmol) was added and the solution changed from yellow to orange. After the mixture was stirred for 21 h under N$_2$, the solvent was removed under reduced pressure and the residue was crystallized from Et$_2$O–hexane to yield a yellow solid (0.20 g, 32%). **11a**: mp 120–122 °C dec; IR (KBr) $\nu_{C=C}$ = 1720, ν_{C-F} = 1288, 1252 cm^{-1}; ^{19}F NMR (C$_6$D$_6$) δ 118.12 (m, F$_2$), 155.74 (m, F$_1$); ^{1}H NMR (C$_6$D$_6$) δ 0.65 (d, P*Me*$_3$, J_{P-H} = 6.2 Hz). Anal. Calcd for $C_{14}H_{18}F_8NiP_2$: C, 36.65; H, 3.95. Found: C, 36.58; H, 4.09.

(1-2:5-6-η-Octafluorocyclooctatetraene)bis(dimethylphenylphosphine)nickel(0) (11b). To a stirred solution of [Ni(COD)$_2$] (0.39 g, 1.4 mmol) in benzene (15 mL) was added PPhMe$_2$ (0.36 mL, 28 mmol). An immediate color change from yellow to red-orange was observed. OFCOT (0.35 g, 1.4 mmol) was added as a solid, and the reaction mixture was stirred under N$_2$ in the dark for 24 h. The solvent was removed under reduced pressure, and the residue was crystallized from toluene–hexane at −20 °C to yield an orange crystalline solid (0.110 g, 30%). **11b**: mp 145–147 °C dec; IR (CH$_2$Cl$_2$) $\nu_{C=C}$ = 1718, ν_{C-F} = 1295, 1260 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 0.86 (d, P*Me*$_2$Ph, J_{P-H} = 7.6 Hz), 7.0 (m, PMe$_2$*Ph*); ^{19}F NMR (C$_6$D$_6$) δ 117.46 (m, F$_2$), 151.62 (m, F$_1$). Anal. Calcd for $C_{24}H_{22}F_8NiP_2$: C, 49.44; H, 3.80. Found: C, 49.30; H, 3.61.

Attempted Reaction of Bis(1,5-cyclooctadiene)nickel(0) with OFCOT and Tricyclohexylphosphine. To a stirred solution of [Ni(COD)$_2$] (0.2, g, 1.0 mmol) in benzene (15 mL) was added OFCOT (0.25 g, 1.0 mmol) followed by tricyclohexylphosphine (0.56 g, 2.0 mmol). The solution slowly turned orange over a span of 8.5 h, but ^{19}F NMR spectroscopy showed only the single resonance of unreacted OFCOT.

Attempted Reaction of Bis(1,5-cyclooctadiene)nickel(0) with OFCOT and Triphenyl Phosphite. To a stirred solution of [Ni(COD)$_2$] (0.40 g, 1.4 mmol) in THF (20 mL) was added OFCOT (0.36 g, 1.4 mmol) followed by P(OPh)$_3$ (1.10 mL, 4.2 mmol). The solution slowly turned orange over a span of 8 h, but ^{19}F NMR spectroscopy showed only the single resonance of unreacted OFCOT.

Attempted Reaction of Bis(1,5-cyclooctadiene)nickel(0) with OFCOT and Trimethyl Phosphite. To a stirred solution of [Ni(COD)$_2$] (0.24 g, 0.87 mmol) in THF (15 mL) was added OFCOT (0.21 g, 0.87 mmol) followed by P(OMe)$_3$ (0.30 mL, 2.6 mmol). The solution darkened over a span of 8 h, but ^{19}F NMR spectroscopy showed only the single resonance of unreacted OFCOT.

Attempted Reaction of Bis(triphenylphosphine)(η-ethylene)nickel with OFCOT. To a stirred solution of [Ni(PPh$_3$)$_2$(C$_2$H$_4$)] (0.20 g, 0.33 mmol) in benzene (15 mL) was added OFCOT (0.081 g, 0.33 mmol). The reaction was stirred at room temperature and monitored by ^{19}F NMR spectroscopy. Only the resonance of OFCOT was present after 21 h. The reaction mixture was heated to reflux for 4 days, resulting in decomposition of the nickel starting material and no loss of OFCOT.

Attempted Reaction of Bis(diphenylmethylphosphine)(η-ethylene)nickel with OFCOT. To a stirred solution of [Ni(PPh$_2$Me)$_2$(C$_2$H$_4$)] (0.42 g, 0.86 mmol) in THF (20 mL) was added OFCOT (0.198 g, 0.80 mmol). The reaction mixture was stirred at room temperature and monitored by ^{19}F NMR spectroscopy. Only the resonance of OFCOT was present after 24 h.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(*tert*-butyl isocyanide)nickel(II) (12). To a stirred solution of [Ni(COD)$_2$] (0.27 g, 0.98 mmol) in THF (10 mL) was added solid OFCOT (0.24 g, 0.98 mmol). *tert*-Butyl isocyanide (0.21 mL, 1.9 mmol) was added via a gastight syringe. The resulting red-orange solution was stirred for 6 h, and then the solvent was removed under reduced pressure. The ^{19}F NMR spectrum of the residue indicated complete conversion to the product **12**. Crystallization of this solid from Et_2O–hexane afforded 0.22 g (48%) of an analytically pure orange crystalline solid. **12**: mp 107–109 °C dec; IR (KBr) $\nu_{N\equiv C}$ = 2192, $\nu_{C=C}$ = 1691 cm^{-1}; ^{19}F NMR (C_6D_6) δ 136.69 (m, F_1), 141.68 (m, F_3), 158.22 (m, F_4), 198.70 (m, F_2, F_5); ^{1}H NMR (C_6D_6) δ 0.85 (s, *Me*$_3$CNC). Anal. Calcd for $C_{18}H_{18}F_8NiN_2$: C, 45.70; H, 3.83; N, 5.92. Found: C, 45.59; H, 3.71; N, 5.84.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(*tert*-butyl isocyanide)(trimethylphosphine)nickel(II) (13a). To a stirred solution of [Ni(COD)$_2$] (0.28 g, 1.0 mmol) in THF (20 mL) was added solid OFCOT (0.28 g, 1.0 mmol). *tert*-Butyl isocyanide (0.23 mL, 2.0 mmol) was added via a gastight syringe, causing a color change from yellow to orange. After 15 min, a ^{19}F NMR spectrum was taken, which indicated clean conversion to **12**. Trimethylphosphine (0.20 mL, 2.0 mmol) was added via a gastight syringe, causing an immediate color change from orange to cherry red. After 10 min, the solvent was removed under reduced pressure, the residue was dissolved in diethyl ether (20 mL), and the resulting solution was filtered through filter pulp. Hexane (20 mL) was layered onto the top of the filtrate, and the solution was cooled to -60 °C. A red crystalline solid was deposited and was collected by filtration (0.24 g, 44%). **13a**: mp 93–97 °C dec; IR (KBr) $\nu_{N\equiv C}$ = 2160, $\nu_{C=C}$ = 1707, 1690 cm^{-1}; ^{19}F NMR (C_6D_6, 20 °C) δ 135.04 (m, F_1), 141.63 (m, F_3), 161.71 (m, F_4), 182.17 (m, F_2), 198.29 (m, F_5); ^{19}F NMR (CD_2Cl_2, -80 °C): δ 127.25 (m, F_1), 135.06 (m, F_3), 158.57 (m, F_4), 173.92 (m, F_2), 193.38 (m, F_5); ^{1}H NMR (C_6D_6, 20 °C) δ 0.90 (s, 18 H, *Me*$_3$CNC), 1.10 (d, 9 H, J_{P-H} = 6.3 Hz, P*Me*$_3$); ^{1}H NMR (CD_2Cl_2, -60 °C) δ 1.34 (s, 18 H, *Me*$_3$CNC), 1.48 (d, J_{P-H} = 7.0 Hz, P*Me*$_3$); ^{31}P NMR (C_6D_6, 20 °C) δ -28.3 (s). Anal. Calcd for $C_{36}H_{33}F_8NiN_2P$: C, 45.93; H, 4.96; N, 5.10. Found: C, 45.56; H, 4.86; N, 4.91.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)bis(*tert*-butyl isocyanide)(triphenylphosphine)nickel(II) (13b). To a stirred solution of [Ni(COD)$_2$] (0.28 g, 1.0 mmol) in THF (20 mL) was added solid OFCOT (0.28 g, 1.0 mmol). *tert*-Butyl isocyanide (0.23 mL, 2.0 mmol) was added via a gastight syringe, causing the solution to change color from yellow to orange. After 30 min, a ^{19}F NMR spectrum was taken, which indicated clean conversion to **12**. Triphenylphosphine (0.26 g, 1.0 mmol) was added as a solid against a backflow of N_2. After 30 min, the solvent was removed from the red solution under reduced pressure, the residue was dissolved in 30 mL of diethyl ether, and the resulting solution was filtered through filter pulp. Hexane (20 mL) was layered onto the top of the filtrate, and the solution was cooled to -20 °C. An orange crystalline solid was deposited, which was collected by filtration (0.35 g, 48%). **13b**: mp 99–103 °C dec; IR (CH_2Cl_2) $\nu_{N\equiv C}$ = 2188, 2197, $\nu_{C=C}$ = 1693, 1704 cm^{-1}; ^{19}F NMR (C_6D_6, 20 °C) δ 136.69 (m, F_1), 141.58 (m, F_3), 158.26 (m, F_4), 197.80 (m, F_2, F_5); ^{19}F NMR (CD_2Cl_2, -80 °C) δ 141.03 (m, F_1), 146.46 (m, F_3), 169.94 (m, F_4), 183.79 (m, F_2), 201.97 (m, F_5; ^{1}H NMR (C_6D_6, 20 °C) δ 0.83 (s, 18 H, *Me*$_3$CNC), 7.21 (m, 15 H, P*Ph*$_3$); ^{1}H NMR (CD_2Cl_2, -60 °C) δ 1.28 (s, 18 H, *Me*$_3$CNC), 7.42 (m, 15 H, P*Ph*$_3$). Anal. Calcd for $C_{36}H_{33}F_8NiN_2P$: C, 59.15; H, 4.55; N, 3.84. Found: C, 59.08; H, 4.60; N, 3.78.

(Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl)tris(*tert*-butyl isocyanide)nickel(II) (13c). To a stirred solution of [Ni(COD)$_2$] (0.54 g, 2.0 mmol) in THF (20 mL) was added solid OFCOT (0.48 g, 2.0 mmol). *tert*-Butyl isocyanide (0.63 mL, 6.0 mmol) was added via a gastight syringe. The solution changed from yellow to cherry red during the addition. After 1 h, the solvent was removed under reduced pressure, the residue was dissolved in 10 mL of diethyl ether, and the resulting solution was filtered through filter pulp. Hexane (20 mL) was layered onto the top of the filtrate, and the solution was cooled to -20 °C. An orange crystalline solid was deposited and collected by filtration (0.48 g, 80%). **13c**: mp 94–101 °C dec; IR (KBr) $\nu_{N\equiv C}$ = 2160, 2182, $\nu_{C=C}$ = 1695, 1688 cm^{-1}; ^{19}F NMR (C_6D_6, 20 °C) δ 135.43 (m, F_1), 142.01 (m, F_3), 161.25 (m, F_4), 184.46 (m, F_2), 199.01 (m, F_5); ^{19}F NMR (CD_2Cl_2, -80 °C) δ 130.22 (m, F_1), 137.47 (m, F_3), 159.57 (m, F_4), 177.26 (m, F_3), 195.90 (m, F_5); ^{1}H NMR (C_6D_6, 20 °C) δ 0.90 (s, *Me*$_3$CNC); ^{1}H NMR (CD_2Cl_2, -60 °C) δ 1.48 (s, *Me*$_3$CNC). Anal. Calcd for $C_{23}H_{27}F_8N_3Ni$: C, 49.67; H, 4.89; N, 7.55. Found: C, 49.62; H, 4.79; N, 7.42.

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