is possible in part because the low effective nuclear charges Z_{eff} of the early transition elements make the d orbitals unusually high in energy. The energies of the d orbitals are raised even higher in $TiMe_2(dmpe)_2$ (but not in the halide or BH_4^- complexes) by the inductive effect of the strongly σ-donating Ti–Me groups. In other words, by acting as strong σ-donors, the methyl groups put more electron density on the titanium center, and the additional electron density helps to screen the nuclear charge.[34] In contrast, halide and BH_4^- groups are poor σ-donors and do not exert as strong an inductive effect. As a result, in $TiMe_2(dmpe)_2$ there is an unusually good match in the energies of the filled d orbitals and the empty P–C σ^* orbitals on the phosphine ligands. Because the b_{2g} (d_{xy}) orbital lies in the plane of the phosphine ligands, it can interact with four such σ^* orbitals, while the e_g (d_{xz} and d_{yz}) orbitals on Ti can interact with only two. Consequently, the b_{2g} orbital is preferentially stabilized (Figure 2c). The amount of π-overlap must be large, since the splitting between the b_{2g} and e_g orbitals is sufficient to cause pairing of the two d electrons of $TiMe_2(dmpe)_2$ in the b_{2g} orbital.[35]

These results add strength to the contention that early transition metals in their lower oxidation states are exceedingly strong π-donors,[1–3,36–38] and can engage in strong π-back-bonding even with normally poor π-acceptors such as trialkylphosphines. This view leads to some interesting predictions: for example, the strongest π-back-bonding between a carbonyl ligand and a transition metal should occur in compounds of low-valent hafnium[39–42] and *not* in compounds of the later transition elements as is commonly thought.[43]

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Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for $Ti(OPh)_2(dmpe)_2$ (4 pages); a table of final observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Excited-State Properties of Mononuclear and Binuclear Rhenium(I) Complexes

The spectroscopic and photophysical properties of oligonuclear complexes containing d^6 metals have received considerable attention of late, in part because of their potential utility in photochemical energy storage systems and as multielectron redox agents. In particular, multinuclear transition-metal-based systems containing ligand bridges have been utilized in a number of studies concerning electron- or energy-transfer reactions.[1–10] Rhenium(I) complexes are especially attractive in this regard, since they are readily synthesized, are chemically stable, and generally possess an extremely high quantum yield for emission.[7–13] However, some of the binuclear complexes of this type, such as the 2,2′-bipyrimidine-bridged compound prepared by Vogler and Kisslinger,[7] are virtually nonemissive. Although those authors suggested that population of a low-lying metal-to-metal charge-transfer excited state was responsible for the lack of luminescence, recent work in our laboratory[9] and elsewhere[5,10] indicates that the perturbation of the π^* orbital on the bridging ligand is of prime importance in determining the photophysical properties of such complexes. Tapolsky et al.[10] have exploited this effect to achieve an "electron/energy-transfer cascade" in the binuclear complex $[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bpy)]^{2+}$, where 4,4′-bpy represents 4,4′-bipyridine and bpy = 2,2′-bipyridine. In this complex, the proximity of the Re → bpy and Re → 4,4′-bpy MLCT levels allows for control of the excited-state properties by variation of

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Table I. Photophysical Data for $[(LL)(CO)_3Re(4,4'\text{-bpy})]^+$ and $[(LL)(CO)_3Re(4,4'\text{-bpy})Re(CO)_3(LL)]^{2+}$[a]

LL[b]	emission max, nm mononuclear	emission max, nm binuclear	lifetime,[c] mononuclear	lifetime,[c] binuclear
5-Cl-phen	579	578	952 (830)	978 (983)
phen	565	564	1520 (1460)	1480 (1420)
5-Mephen	564	564	1893	1010
4-Mephen	558	558	2700 (2210)	845 (950)
5,6-Me_2phen	559	558	3900	1563
4,7-Me_2phen	547	564	4550 (*d*)	593 (623)
3,4,7,8-Me_4phen	526	620	15000 (*e*)	595[f] (483)

[a] All data recorded in CH_3CN; $T = 298 \pm 1$ K for emission measurements; $T = 294 \pm 1$ K for TA experiments; experimental details provided in ref 10. [b] Abbreviations are as follows: phen = 1,10-phenanthroline; Cl-phen = chlorophenanthroline; Mephen = methyl-1,10-phenanthroline; Me_2phen = dimethyl-1,10-phenanthroline; Me_4phen = tetramethyl-1,10-phenanthroline; positions of substituents are as indicated. [c] Unbracketed values represent emission lifetimes, λ_{ex} = 355 nm. Numbers in parentheses refer to lifetimes measured by transient absorption (TA), λ_{ex} = 355 nm. All lifetimes are ±5% unless otherwise noted. [d] TA lifetimes for this complex were somewhat sensitive to experimental conditions, including laser power. In general, lifetimes of 3600–4500 ns were obtained. [e] Lifetime of transient was too long for accurate measurement by TA using available instrumentation. [f] Very weak emission; reported lifetime is ±10%.

solvent polarity. At the same time, our work in progress suggested that similar "fine-tuning" of excited-state energies and behavior could be achieved by utilizing a series of substituted 1,10-phenanthrolines as the chelating ligands, and this communication describes our initial experiments using such an approach. The preparation and characterization of these complexes will be reported in a forthcoming full paper.

Emission spectra and lifetimes of the complexes $[(CO)_3(LL)Re(4,4'\text{-bpy})]^+$ (where LL = 1,10-phenanthroline or a suitably substituted derivative), as well as those of the corresponding binuclear species, were acquired in room-temperature deoxygenated CH_3CN, and the relevant data are collected in Table I. All mononuclear complexes display an extremely intense unstructured emission that is clearly visible with the naked eye, and the observed emission energy is a sensitive function of substituent. The mononuclear species exhibit a first-order decay profile at room temperature, and the emission can be confidently assigned to the Re → LL MLCT state.[8-13] Transient absorption (TA) measurements confirm the Re → LL MLCT assignment, showing a broad, intense absorption at 410–450 nm (Figure 1). This peak has been previously shown to arise from a $\pi \rightarrow \pi^*$ (phen$^{\bullet -}$) transition.[13] The TA spectra of these complexes display wavelength-independent first-order kinetics, and the measured excited-state lifetimes are consistent (within 10%) with those found in the time-resolved emission studies.

The emission lifetimes of the phenanthroline complexes are considerably longer than those that have been reported for structurally similar bpy derivatives and increase dramatically with increasing electron donation from methyl substituents. In fact, the lifetime of $[(CO)_3(3,4,7,8\text{-}Me_4phen)Re(4,4'\text{-bpy})]^+$ reaches the remarkable value of 15 μs in room temperature CH_3CN, over 60 times longer than that of the analogous bpy complex.[9,10,14] These results are qualitatively expected from consideration of the energy gap law, which has already been shown to be operative in a series of closely related rhenium complexes.[12]

On the other hand, the binuclear complexes (with the exception of $[(5\text{-Cl-phen})(CO)_3Re(4,4'\text{-bpy})Re(CO)_3(5\text{-Cl-phen})]^{2+}$) exhibit significantly different behavior than their mononuclear counterparts, and a comparison of TA spectra suggests that the underlying reason for such differences is a change in the nature of the lowest lying excited state. Rather than the single 410–450-nm band, which is characteristic of a Re → LL MLCT state, the TA spectra of these complexes display two major features, centered at 400 and 600 nm (see Figure 2). Such behavior is consistent with population of the Re → 4,4′-bpy MLCT state,[15] and indicates that the energy of this state falls below that of the Re → LL level upon attachment of the second metal center. However, the energies of the two relevant MLCT states are apparently very similar in most of the binuclear complexes, as the observed emission maxima closely parallel those of the corresponding mononuclear species, except where LL = 4,7-Me_2phen or 3,4,7,8-Me_4phen. For these two complexes, the emission maxima are observed at significantly longer wavelengths, with the difference amounting to nearly 100 nm in the Me_4phen case. In addition, the excited-state lifetime decreases with increasing methyl substitution, a trend which is essentially the opposite of that seen in the mononuclear species. Again, this trend is in accord with the energy gap law, since the increasing electron density on the metal center is expected to lower the Re → 4,4′-bpy transition energy.[16]

In contrast, the dominant effect of added methyl substituents on the Re → LL MLCT level appears to be an increase in energy

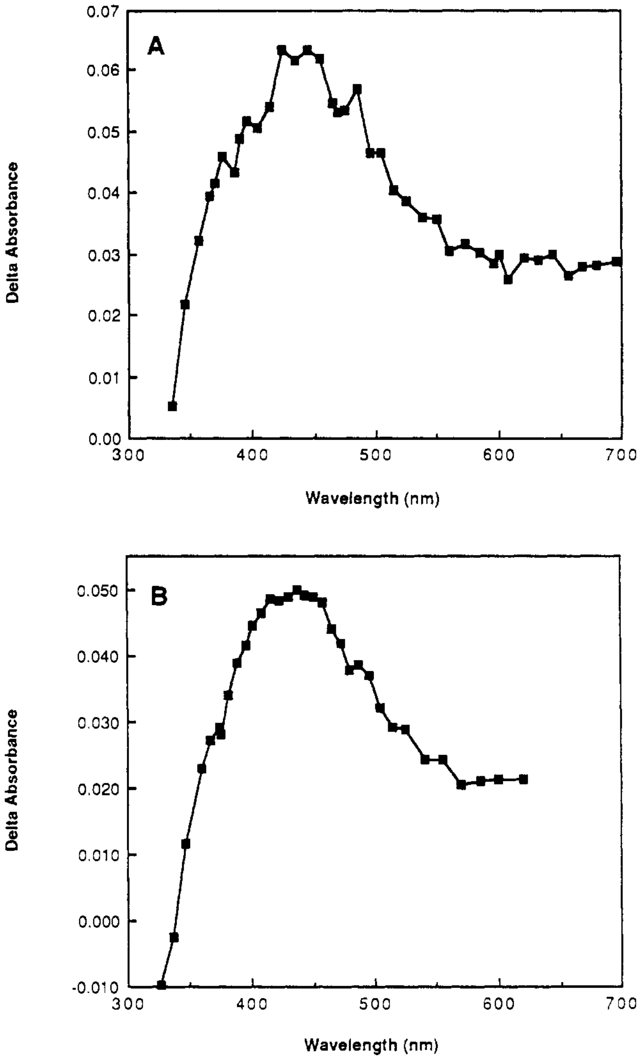

Figure 1. Transient absorbance difference spectra obtained 25 ns after 355-nm laser excitation in freeze–pump–thaw-deoxygenated acetonitrile solutions at 294 ± 1 K: (A) $[(phen)(CO)_3Re^I(4,4'\text{-bpy})]^+$; (B) $[(4\text{-Mephen})(CO)_3Re^I(4,4'\text{-bpy})]^+$.

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(16) The experimentally observed $Re^{I/II}$ oxidation potentials appear to bear out this expectation, as anodic peak potentials shift to less positive values upon increasing methyl substitution. The magnitude of the shift corresponds to roughly 15 mV per methyl group.

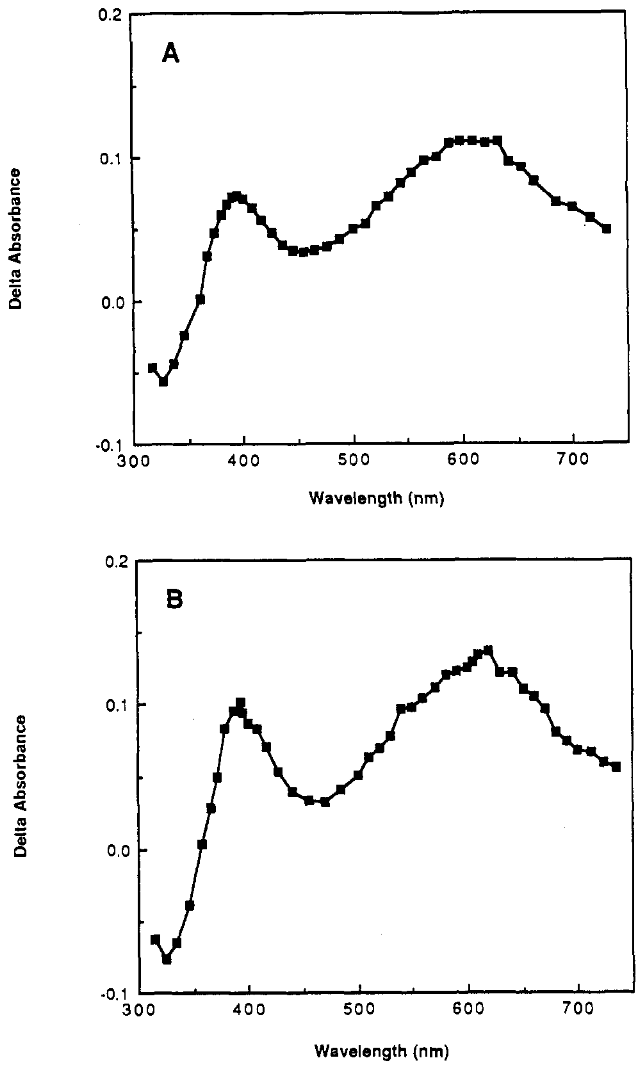

Figure 2. Transient absorbance difference spectra obtained 25 ns after 355 nm laser excitation in freeze–pump–thaw-deoxygenated acetonitrile solutions at 294 ± 1 K: (A) $[(4\text{-Mephen})(CO)_3Re^I(4,4'\text{-bpy})Re^I(CO)_3(4\text{-Mephen})]^{2+}$; (B) $[(3,4,7,8\text{-Me}_4\text{phen})(CO)_3Re^I(4,4'\text{-bpy})Re^I(CO)_3(3,4,7,8)\text{-Me}_4\text{phen})]^{2+}$.

caused by the increasing energy of the π^* orbital on LL. This is evidenced by electrochemical measurements in dimethyl sulfoxide,[17] which reveal that the LL reduction shifts to more negative potentials upon increasing methyl substitution. Thus, the reduction potentials of the phen and methyl-substituted phen ligands range from −1.07 to −1.32 V vs SCE, depending on the number and position of the methyl substituents. Meanwhile, each of the binuclear complexes displays a one-electron reduction at −0.96 ± 0.03 V vs SCE, and this process is assigned to the reduction of the 4,4′-bpy ligand. These results support the notion that the bridge-based state will likely represent the lowest energy excited state for all of the bimetallic complexes that possess electron-donating substituents.

In the case of the binuclear 5-Cl-phen derivative, however, the first reduction is centered on the chelating ligand ($E^{red}_{1/2} = -0.90$ V for 5-Cl-phen vs −0.95 V for 4,4′-bpy). The emission lifetimes of the mononuclear and binuclear 5-Cl-phen complexes are virtually identical, and the TA spectra (Figure 3) are indicative of a common excited state (the Re → 5-Cl-phen MLCT level). Still, the extensive tailing at longer wavelengths in the TA spectrum of the binuclear species suggests that some population of the Re → 4,4′-bpy level may also be occurring. Nevertheless, it seems clear that the addition of the Cl substituent causes an inversion (as compared to LL = phen) in the energies of the two lowest lying MLCT states under these experimental conditions.[18]

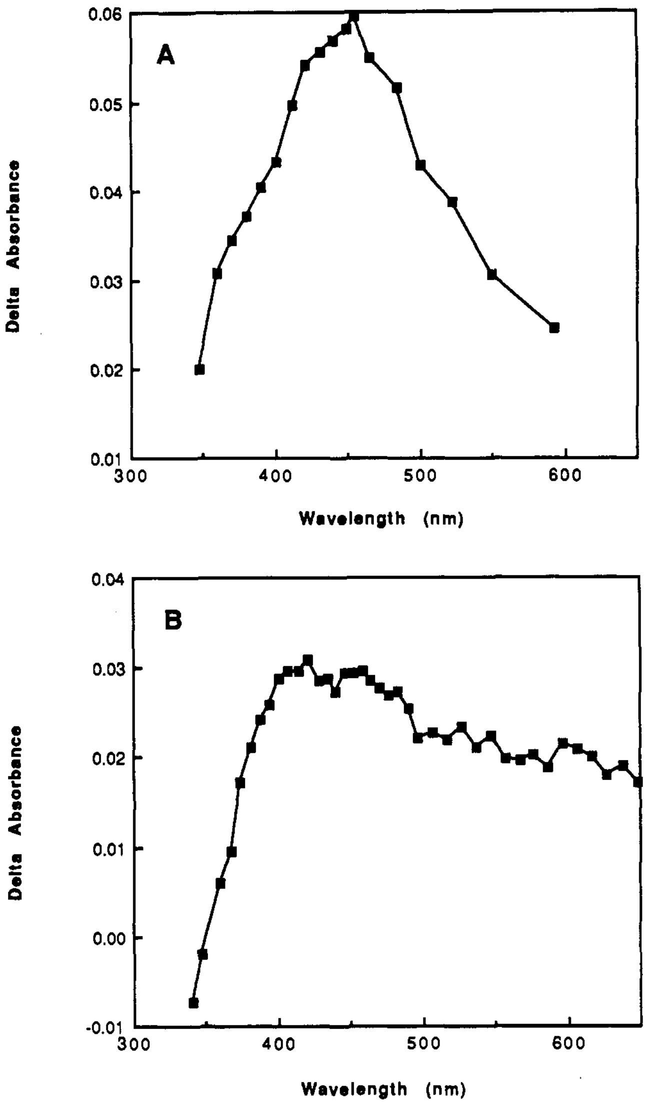

Figure 3. Transient absorbance difference spectra obtained 35 ns after 355 nm laser excitation in freeze–pump–thaw-deoxygenated acetonitrile solutions at 294 ± 1 K: (A) $[(5\text{-Cl-phen})(CO)_3Re^I(4,4'\text{-bpy})]^+$; (B) $[(5\text{-Cl-phen})(CO)_3Re^I(4,4'\text{-bpy})Re^I(CO)_3(5\text{-Cl-phen})]^{2+}$.

In summary, the available data are consistent with a model in which there are two potentially emissive MLCT excited-state manifolds, one involving the phenanthroline chelate and the other involving the 4,4′-bpy bridging ligand. Interconversion between the two manifolds is rapid, so that emission is generally observed only from the lowest lying level. Attachment of a second metal center to the 4,4′-bpy ligand significantly decreases the energy of the π^* orbital on the bridge, thus dropping the energy of the bridge-based MLCT. The relative position of the two levels can be further controlled by substituent effects: increasing methyl substitution on LL raises the Re → LL state while lowering the Re → 4,4′-bpy state. As a result, the lowest excited state in all binuclear complexes except the 5-Cl-phen derivative is the Re → 4,4′-bpy MLCT level.

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(17) Reduction potentials of the binuclear complexes could not be accurately measured in acetonitrile owing to adsorption effects.

(18) It should be emphasized that, despite the close correlation between mononuclear and binuclear phen complexes in terms of emission maxima and lifetimes, the TA spectra provide unambiguous evidence for a Re → phen state in the former and a Re → 4,4′-bpy state in the latter.

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Oxidative Addition of N–H Bonds to Iridium: Synthesis and Structure of (Heterocyclic amine)iridium Hydride Complexes

While the area of C–H activation chemistry has attracted a great deal of activity over the past several years,[1] there has been much less effort devoted to examining N–H bond activation in spite of the possibilities for developing systems for the catalytic functionalization of ammonia and other amines. Examples in the literature of oxidative-addition reactions of N–H bonds with transition-metal complexes are rare,[2] many dealing with chelate-assisted N–H bond addition. Recently, the addition of amide N–H bonds to low-valent Fe and Ru compounds was reported,[3] but the most intriguing reports to date have come from Du Pont Central Research, where oxidative-addition of NH_3 and aniline was demonstrated, the latter as part of a catalyst system capable of adding aniline to norbornene.[4] Recently we have reported the oxidative addition of aromatic C–H bonds to Ir using $[Ir(COD)PMe_3)_3]Cl$ (COD = cyclooctadiene) and the further reactions of the resulting iridium hydride complexes with alkynes.[5] We believed that this iridium system would provide us with an ideal opportunity to examine the general reactions of a series of E–H compounds with iridium (E = C, B, H, Al, Si) and the reactivity of the resulting hydrides. In a separate paper we have reported some results with B–H compounds,[6] and in this paper we discuss our initial results with N–H compounds.

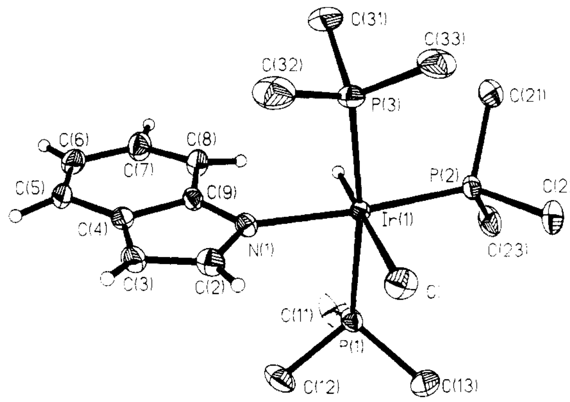

Figure 1. ORTEP plot of **1b** (PMe_3 hydrogen atoms omitted for clarity). Important bond distances (Å): Ir(1)–Cl, 2.491 (2); Ir(1)–P(1), 2.326 (2); Ir(1)–P(2), 2.271 (2); Ir(1)–P(3), 2.335 (2); Ir(1)–N(1), 2.131 (4); Ir(1)–H(1), 1.489 (49). Important bond angles (deg): Cl–Ir(1)–P(1), 89.1 (1); Cl–Ir(1)–P(2), 96.0 (1); P(1)–Ir(1)–P(2), 95.0 (1); Cl–Ir(1)–P(3), 88.7 (1); P(1)–Ir(1)–P(3), 170.6 (1); P(2)–Ir(1)–P(3), 94.4 (1); Cl–Ir(1)–N(1), 91.6 (1); P(1)–Ir(1)–N(1), 85.7 (1); P(2)–Ir(1)–N(1), 172.3 (1); P(3)–Ir(1)–N(1), 85.2 (1); Cl–Ir(1)–H(1), 179.0 (19); P(1)–Ir(1)–H(1), 91.6 (20); P(2)–Ir(1)–H(1), 84.6 (18); P(3)–Ir(1)–H(1), 90.5 (20); N(1)–Ir(1)–H(1), 87.7 (18).

Heating $[Ir(COD)(PMe_3)_3]Cl$[7] with the heterocyclic amines pyrrole,[8] indole,[9] 3-methylindole,[10] and 7-azaindole[11] leads to the

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[8] A 0.42-g (0.75-mmol) quantity of $[Ir(COD)(PMe_3)_3]Cl$ was dissolved in 2.0 mL of dry pyrrole, and the mixture was refluxed under N_2 for 16 h. A small amount of solid was filtered out, and the pyrrole was removed under reduced pressure to yield a brown oil. The oil was dissolved in 5 mL of dry THF, and the mixture was then concentrated to 0.5 mL and treated with 2 mL of dry pentane to crystallize pale yellow solids. The solids were collected and dried to yield 0.36 g (0.69 mmol, 93%) of $Ir(PMe_3)_3(Cl)(H)(NC_4H_4)$ (**1a**), identified on the basis of the following information. ^1H NMR (270 MHz at 20 °C in $CDCl_3$): δ −22.12 (dt, J_{P-H} = 17, 15 Hz, 1 H, Ir–H), 1.28 (t, J_{P-H} = 3.6 Hz, 18 H, trans PMe_3), 1.65 (d, J_{P-H} = 9.4 Hz, cis PMe_3), 5.98–5.99 (m, 2 H, H(3) and H(4), NC_4H_4), 6.39 (m, 1 H, H(5), NC_4H_4), 7.18 ppm (m, 1 H, H(2), NC_4H_4). $^{31}P\{^1H\}$ NMR (81 MHz at 20 °C in $CDCl_3$): δ −50.85 (vbr, 1 P, cis PMe_3), −34.02 ppm (d, J_{P-P} = 42 Hz, 2 P, trans PMe_3). ^{13}C NMR (50 MHz at 20 °C in $CDCl_3$): δ 15.88 (t, J_{P-C} = 18.3 Hz, trans PMe_3), 20.48 (d, J_{P-C} = 37 Hz, cis PMe_3), 104.2, 106.9, 128.6, 135.1 ppm (all s, NC_4H_4). Anal. Calcd (found): C, 29.86 (29.92); H, 6.17 (6.19). IR (CH_2Cl_2) ν_{Ir-H} = 2168 cm^{-1}.

[9] A suspension of 1.0 g (1.78 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ and 0.208 (1.78 mmol) of indole was refluxed under N_2 in 4 mL of dry mesitylene for 18 h. After 18 h, the mixture was a pale pink solution with off-white solids suspended. The precipitate was filtered out, washed with pentane, and dried to yield 0.70 g (1.21 mmol, 68%) of $Ir(PMe_3)_3(H)(Cl)(NC_8H_6)$ (**1b**), identified on the basis of the following information. ^1H NMR (270 MHz at 20 °C in acetone-d_6): δ −20.86 (dt, J_{P-H} = 16, 14 Hz, 1 H, Ir–H), 1.15 (t, J_{P-H} = 3.6 Hz, 18 H, trans PMe_3), 1.79 (d, J_{P-H} = 9.8 Hz, cis PMe_3), 6.24 (d, J = 1.2 Hz, 1 H, H(3), NC_8H_6), 6.67 (dt, J = 7.7, 0.9 Hz, 1 H, H(5), NC_8H_6), 6.78–6.84 (m, 1 H, H(6), NC_8H_6), 7.34 (dd, J = 7.7, 0.6 Hz, 1 H, H(7), NC_8H_6), 7.43 (dd, J = 8.3, 0.6 Hz, 1 H, H(4), NC_8H_6), 8.04–8.03 ppm (m, 1 H, H(2), NC_8H_6). $^{31}P\{^1H\}$ NMR (81 MHz at 20 °C in $CDCl_3$): δ −49.44 (br t, J_{P-P} = 22 Hz, 1 P, cis PMe_3), −33.70 ppm (d, J_{P-P} = 21 Hz, 2 P, trans PMe_3). Anal. Calcd (found): C, 35.63 (35.36); H, 5.98 (5.85). IR (CH_2Cl_2): ν_{Ir-H} = 2221 cm^{-1}.

[10] A suspension of 0.25 g (0.44 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ and 0.064 g (0.49 mmol) of 3-methylindole was refluxed under N_2 in 3 mL of mesitylene for 15 h. After 15 h, the reaction mixture was a brown solution with a white precipitate. The precipitate was collected and washed with pentane to yield 0.16 g (0.27 mmol, 62%) of $Ir(PMe_3)_3(H)(Cl)(NC_9H_8)$ (**1c**), identified on the basis of the following information. ^1H NMR (270 MHz at 20 °C in acetone-d_6): δ −20.92 (q, J_{P-H} = 16 Hz, 1 H, Ir–H), 1.14 (t, J_{P-H} = 3.6 Hz, 18 H, trans PMe_3), 1.78 (d, J_{P-H} = 9.8 Hz, cis PMe_3), 2.31 (s, 3 H, 3-methyl), 6.63–6.84 (m, 2 H, H(5) and H(6), NC_9H_8), 7.25–7.35 (m, 2 H, H(4) and H(7), NC_9H_8), 7.81 ppm (s, 1 H, H(2), NC_9H_8). $^{31}P\{^1H\}$ NMR (81 MHz at 20 °C in $CDCl_3$): δ −49.00 (br t, J_{P-P} = 22 Hz, 1 P, cis PMe_3), −33.42 ppm (d, J_{P-P} = 21 Hz, 2 P, trans PMe_3). Anal. Calcd (found): C, 36.83 (36.86); H, 6.18 (6.22). IR (CH_2Cl_2): ν_{Ir-H} = 2180 cm^{-1}.

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