Table S6: EXAFS Curve Fitting Results from *Chromatium vinosum* Hydrogenase Form R.[a]

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
1	4	Ni – O = 2.0241(2)	2.4	-2.2	55.2
	5	Ni – O = 2.0211(2)	4.4	-0.2	60.9
	6	Ni – O = 2.0180(2)	6.4	1.8	64.9
	4	Ni – S = 2.2004(2)	7.2	4.7	22.5
	5	Ni – S = 2.2027(2)	9.2	6.7	23.9
	6	Ni – S = 2.2045(2)	11.0[b]	8.5	26.0
2	1	Ni – O = 1.918(5)	24.3	19.7	21.7
	3	Ni – S = 2.1987(2)	5.1	2.6	
	2	Ni – O = 1.949(1)	14.9	10.3	21.4
	2	Ni – S = 2.1984(2)	2.6	0.1	
	1	Ni – O = 1.559(3)	22.6	18.0	22.5
	4	Ni – S = 2.1994(2)	7.2	4.7	
	2	Ni – O = 1.860(6)	47.7	43.1	21.7
	3	Ni – S = 2.1981(2)	5.0	2.5	
	1	Ni – O = 1.598(2)	20.0	15.4	23.6
		Ni – S = 2.2011(2)	9.2	6.7	
	2	Ni – O = 1.600(5)	126.5	119.9	22.3
	4	Ni – S = 2.1990(2)	7.1	4.6	

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	4	Ni – S = 2.1997(2)	7.4	4.9	19.3
	1	Ni – Fe = 2.8726(8)	7.6	6.1	
	5	Ni – S = 2.2022(2)	9.4	6.9	20.2
	1	Ni – Fe = 2.8716(8)	7.8	6.3	
	6	Ni – S = 2.2041(2)	11.2	8.7	22.0
	1	Ni – Fe = 2.8698(8)	8.0	6.5	
	4	Ni – S = 2.1895(2)	7.0	4.5	12.4
	1	Ni – Fe = 2.5354(3)	5.1	3.6	
	5	Ni – S = 2.1918(2)	9.3	6.8	16.8
	1	Ni – Fe = 2.5399(4)	6.2	4.7	
	6	Ni – S = 2.1941(2)	11.7	9.2	21.9
	1	Ni – Fe = 2.5300(6)	8.2	6.7	
	1	Ni – S = 2.1405(4)	0.9	-1.6	23.3
	3	Ni – S = 2.2453(3)	5.4	2.9	
	2	Ni – S = 2.1597(2)	1.2	-1.3	23.5
	2	Ni – S = 2.2904(3)	2.3	-0.2	

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	3	Ni – S = 2.1876(2)	2.5	0	22.3
	1	Ni – S = 2.3388(3)	-0.9	-3.4	
	1	Ni – S = 2.1963(5)	3.2	0.7	23.0
	4	Ni – S = 2.2045(5)	12.0	9.5	
	2	Ni – S = 2.156(1)	5.8	3.3	24.1
	3	Ni – S = 2.2479(9)	7.6	5.1	
	3	Ni – S = 2.1701(2)	3.7	1.2	24.9
	2	Ni – S = 2.3081(3)	3.4	0.9	
	4	Ni – S =	No Fit		
	1	Ni – S =			
	1	Ni – S = 1.921(2)	20.0	17.5	23.1
	5	Ni – S = 2.1983(2)	8.7	6.2	
	2	Ni – S = 1.893(5)	51.6	49.1	22.6
	4	Ni – S = 2.1992(2)	7.1	4.6	
	3	Ni – S = 2.188(4)	54.7	52.2	21.1
	3	Ni – S = 2.1979(2)	5.1	2.6	

Table S6

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	4	Ni – S = 2.1760(4)	7.9	5.4	26.4
	2	Ni – S = 2.292(1)	7.4	4.9	
	5	Ni – S = 2.1977(2)	9.7	7.2	16.4
	1	Ni – S = 2.6803(5)	2.4	-0.1	
	1	Ni – C = 1.598(4)	16.5	11.4	22.0
	3	Ni – S = 2.1972(2)	5.0	2.5	
	1	Ni – C = 1.666(4)	21.4	16.3	22.5
	4	Ni – S = 2.1995(2)	7.2	4.7	
	1	Ni – C = 1.770(1)	8.9	3.8	23.1
	5	Ni – S = 2.1994(2)	9.1	6.6	
	1	Ni – S =	No Fit		
	3	Ni – S =			
	1	Ni – Fe =			
	2	Ni – S = 2.1831(1)	1.9	-0.6	6.0
	2	Ni – S = 2.37(2)	71.3	68.8	
	1	Ni – Fe = 2.5105(3)	3.6	2.1	

Table S6

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	3	Ni – S = 2.1942(2)	4.4	1.9	4.6
	1	Ni – S = 2.614(1)	-2.1	-4.6	
	1	Ni – Fe = 2.5959(8)	1.7	0.2	

[a]Fits were generated using k^3 Fourier-filtered data (FT = 2 – 14.3 Å^{-1}, BT = 1.1 – 2.6 Å, uncorrected for phase shifts). σ^2 is the root mean square disorder in the Ni-X distance; $\Delta\sigma^2$ is σ^2 relative to calculated values for reference compounds; GOF = $1/\sigma^2 \sum_{i=1}^{N} \left[y_{\exp}(i) - y_{theo}(i) \right]^2$ (see text). The accuracy of distances determined by EXAFS for atoms in the first coordination sphere of the metal are limited to ± 0.02 Å by the theoretical phase parameters. The refinements generally show precisions that are less than 0.02 Å for well-ordered shells, thus differences in distances between samples using equivalent fits are more accurate than the absolute distances. [b] Underlined values are approaching physical insignificance. Large values of σ^2 suggest that the shell involved has a coordination number that is too large or is badly disordered.

Table S7: EXAFS Curve Fitting Results from *Chromatium vinosum* Hydrogenase Form L.[a]

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
1	4	Ni – O = 2.0513(1)	3.0	-1.6	52.6
	5	Ni – O = 2.0486(1)	5.0	0.4	58.1
	6	Ni – O = 2.0455(1)	7.0	2.4	62.1
	4	Ni – S = 2.2352(1)	7.7	5.2	15.4
	5	Ni – S = 2.2372(1)	9.8	7.3	16.3
	6	Ni – S = 2.2387(1)	11.6[b]	9.1	18.4
2	1	Ni – O = 1.9697(6)	12.5	7.9	15.7
	3	Ni – S = 2.2371(1)	5.8	3.3	
	2	Ni – O = 1.9826(2)	11.1	6.5	17.6
	2	Ni – S = 2.2385(1)	3.3	0.8	
	1	Ni – O =	No Fit		
	4	Ni – S =			
	2	Ni – O = 1.9511(7)	27.2	22.6	15.4
	3	Ni – S = 2.2354(1)	5.7	3.2	
	1	Ni – O =	No Fit		
	5	Ni – S =			
	2	Ni – O =	No Fit		
	4	Ni – S =			

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	4	Ni – S = 2.2344(1)	7.9	5.4	9.8
	1	Ni – Fe = 2.9382(2)	7.7	6.2	
	5	Ni – S = 2.2363(1)	9.9	7.4	10.1
	1	Ni – Fe = 2.9385(2)	8.1	6.6	
	6	Ni – S = 2.2378(1)	11.8	9.3	11.8
	1	Ni – Fe = 2.9372(2)	8.3	6.8	
	4	Ni – S = 2.2249(1)	8.1	5.6	7.2
	1	Ni – Fe = 2.5603(1)	7.9	6.4	
	5	Ni – S = 2.2283(1)	10.6	8.1	11.4
	1	Ni – Fe = 2.5505(2)	10.2	8.7	
	6	Ni – S = 2.2427(1)	12.9	10.4	14.1
	1	Ni – Fe = 2.4516(4)	13.5	12.0	
	1	Ni – S = 2.1577(1)	1.7	-0.8	15.4
	3	Ni – S = 2.2742(1)	5.0	2.5	
	2	Ni – S = 2.1838(1)	2.6	0.1	15.2
	2	Ni – S = 2.3090(1)	2.8	0.3	

Table S7

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	3	Ni – S = 2.2109(1)	4.0	1.5	14.7
	1	Ni – S = 2.3471(1)	0.5	-2.0	
	1	Ni – S = 2.1401(7)	25.7	23.2	15.5
	4	Ni – S = 2.2382(1)	7.9	5.4	
	2	Ni – S = 2.194(1)	9.3	6.8	16.1
	3	Ni – S = 2.2629(9)	8.3	5.8	
	3	Ni – S = 2.1967(1)	6.7	4.2	16.1
	2	Ni – S = 2.3091(2)	5.5	3.0	
	4	Ni – S = 2.2353(1)	7.7	5.2	15.3
	1	Ni – S = 2.4(4)	288.1	285.6	
	1	Ni – S = 1.9410(9)	29.0	26.5	15.6
	5	Ni – S = 2.2348(1)	9.5	7.0	
	2	Ni – S = 1.925(5)	92.3	89.8	15.5
	4	Ni – S = 2.2350(1)	7.7	5.2	
	3	Ni – S = 2.1980(3)	22.2	19.7	16.3
	3	Ni – S = 2.2425(1)	6.9	4.4	

Table S7

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	4	Ni – S = 2.2181(2)	16.4	13.9	17.1
	2	Ni – S = 2.2480(1)	6.2	3.7	
	5	Ni – S = 2.2333(1)	10.2	7.7	7.4
	1	Ni – S = 2.7272(2)	4.8	2.3	
3	1	Ni – S = 2.538(2)	32.3	29.8	5.2
	3	Ni – S = 2.2222(1)	5.5	3.0	
	1	Ni – Fe = 2.5537(1)	6.3	4.8	
	2	Ni – S = 2.2168(1)	3.7	1.2	4.9
	2	Ni – S = 2.2627(6)	22.0	19.5	
	1	Ni – Fe = 2.5372(2)	6.3	4.8	
	3	Ni – S = 2.2222(1)	5.5	3.0	5.2
	1	Ni – S = 2.538(2)	32.3	29.8	
	1	Ni – Fe = 2.5537(1)	6.3	4.8	
	1	Ni – S =	No Fit		
	4	Ni – S =			
	1	Ni – Fe =			
	2	Ni – S = 2.534(2)	44.2	41.7	5.2
	3	Ni – S = 2.2222(1)	5.5	3.0	
	1	Ni – Fe = 2.5534(1)	6.4	4.9	

Table S7

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	3	Ni – S = 2.2222(1)	5.5	3.0	5.2
	2	Ni – S = 2.534(2)	<u>44.2</u>	41.7	
	1	Ni – Fe = 2.5534(1)	6.4	4.9	

[a]Fits were generated using k^3 Fourier-filtered data (FT = 2 – 14.3 Å^{-1}, BT = 1.1 – 2.6 Å, uncorrected for phase shifts). σ^2 is the root mean square disorder in the Ni-X distance; $\Delta\sigma^2$ is σ^2 relative to calculated values for reference compounds; $\mathrm{GOF} = 1/\sigma^2 \sum_{i=1}^{N}\left[y_{\exp}(i) - y_{theo}(i)\right]^2$ (see text). The accuracy of distances determined by EXAFS for atoms in the first coordination sphere of the metal are limited to ± 0.02 Å by the theoretical phase parameters. The refinements generally show precisions that are less than 0.02 Å for well-ordered shells, thus differences in distances between samples using equivalent fits are more accurate than the absolute distances. [b] Underlined values are approaching physical insignificance. Large values of σ^2 suggest that the shell involved has a coordination number that is too large or is badly disordered.

Table S8: EXAFS Curve Fitting Results from *Chromatium vinosum* Hydrogenase Form SI-CO.[a]

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
1	4	Ni – O = 2.0933(2)	2.7	-1.9	58.6
	5	Ni – O = 2.0918(2)	4.6	0	64.2
	6	Ni – O = 2.0899(2)	6.6	2.0	68.5
	4	Ni – S = 2.2770(2)	7.3	4.8	20.2
	5	Ni – S = 2.2785(2)	9.2	6.7	22.0
	6	Ni – S = 2.2797(2)	11.0[b]	8.5	24.9
2	1	Ni – O = 1.704(2)	15.0	10.4	18.3
	3	Ni – S = 2.2732(2)	5.1	2.6	
	2	Ni – O = 2.032(2)	13.2	8.6	24.0
	2	Ni – S = 2.2786(3)	2.9	0.4	
	1	Ni – O = 1.724(2)	12.2	7.6	16.8
	4	Ni – S = 2.2744(2)	7.2	4.7	
	2	Ni – O = 1.759(4)	38.9	34.3	19.0
	3	Ni – S = 2.2746(2)	5.1	2.6	
	1	Ni – O = 1.736(1)	10.4	5.8	17.0
	5	Ni – S = 2.2751(2)	9.2	6.7	
	2	Ni – O = 1.706(2)	22.5	17.9	17.0
	4	Ni – S = 2.2745(2)	7.2	4.7	

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	4	Ni – S = 2.2764(2)	7.4	4.9	16.5
	1	Ni – Fe = 2.999(2)	10.0	8.5	
	5	Ni – S = 2.2778(2)	9.4	6.9	17.7
	1	Ni – Fe = 3.003(2)	10.2	8.7	
	6	Ni – S = 2.2790(2)	11.2	8.7	20.1
	1	Ni – Fe = 3.005(2)	10.5	9.0	
	4	Ni – S = 2.2698(3)	8.5	6.0	13.0
	1	Ni – Fe = 2.550(1)	10.2	8.7	
	5	Ni – S = 2.2775(4)	10.8	8.3	13.9
	1	Ni – Fe = 2.513(2)	11.7	10.2	
	6	Ni – S = 2.2839(4)	12.9	10.4	15.1
	1	Ni – Fe = 2.488(1)	10.0	8.5	
	1	Ni – S = 2.1817(4)	0	-2.5	15.3
	3	Ni – S = 2.3150(2)	3.0	0.5	
	2	Ni – S = 2.2148(3)	2.0	-0.5	14.5
	2	Ni – S = 2.3448(3)	1.2	-1.3	

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	3	Ni – S = 2.2436(3)	4.1	1.6	13.9
	1	Ni – S = 2.3711(4)	-0.4	-2.9	
	1	Ni – S = 2.1713(6)	3.0	0.5	18.9
	4	Ni – S = 2.3054(3)	5.9	3.4	
	2	Ni – S = 2.2018(4)	4.3	1.8	18.1
	3	Ni – S = 2.3291(4)	4.3	1.8	
	3	Ni – S = 2.2273(3)	5.7	3.2	17.5
	2	Ni – S = 2.3501(5)	3.2	0.7	
	4	Ni – S =	No Fit		
	1	Ni – S =			
	1	Ni – S = 1.977(1)	14.5	12.0	16.5
	5	Ni – S = 2.2702(3)	8.8	6.3	
	2	Ni – S = 2.048(3)	35.0	32.5	18.1
	4	Ni – S = 2.2764(2)	7.1	4.6	
	3	Ni – S = 2.197(1)	27.3	24.8	21.7
	3	Ni – S = 2.2819(3)	5.6	3.1	

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	4	Ni – S = 2.2421(7)	14.4	11.9	21.9
	2	Ni – S = 2.3035(8)	5.5	3.0	
	5	Ni – S =	No Fit		
	1	Ni – S =			
	1	Ni – C = 1.7841(9)	4.3	-0.8	16.7
	3	Ni – S = 2.2732(2)	5.3	2.8	
	1	Ni – C = 1.7948(8)	4.5	-0.6	15.6
	4	Ni – S = 2.2737(2)	7.5	5.0	
	1	Ni – C = 1.8050(8)	4.1	-1.0	16.8
	5	Ni – S = 2.2737(2)	9.5	7.0	
3	1	Ni – S = 1.934(1)	16.1	13.6	10.9
	3	Ni – S = 2.2564(3)	5.9	3.4	
	1	Ni – Fe = 2.5581(7)	7.1	5.6	
	2	Ni – S = 2.2218(5)	3.8	1.3	12.2
	2	Ni – S = 2.3434(8)	4.0	1.5	
	1	Ni – Fe = 2.529(2)	12.0	10.5	

Table S8

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	3	Ni – S = 2.2636(3)	5.8	3.3	13.5
	1	Ni – S = 1.91(2)	76.5	74.1	
	1	Ni – Fe = 2.5684(7)	7.6	6.1	
	1	Ni – S = 1.417(2)	21.9	19.4	10.2
	4	Ni – S = 2.2687(3)	8.6	6.1	
	1	Ni – Fe = 2.551(1)	10.0	8.5	
	2	Ni – S = 2.019(6)	48.1	45.6	12.4
	3	Ni – S = 2.2630(3)	5.8	3.3	
	1	Ni – Fe = 2.5648(7)	7.6	6.1	
	3	Ni – S = 2.2630(3)	5.8	3.3	12.4
	2	Ni – S = 2.019(6)	48.1	45.6	
	1	Ni – Fe = 2.5648(7)	7.6	6.1	
	1[c]	Ni – C = 1.7850(9)	4.5	-0.6	16.6
	1	Ni – O = 2.960(2)	626.0	620.6	
	3	Ni – S = 2.2731(2)	5.3	2.8	
	1[c]	Ni – C =	No Fit		
	4	Ni – O =			
	1	Ni – S =			

Table S8

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	1[c]	Ni – C =	No Fit		
	1	Ni – O =			
	5	Ni – S =			
	1[d]	Ni – C = 1.7827(9)	3.8	-1.3	11.6
	1	Ni – O = 2.7826(9)	6.2	0.8	
	3	Ni – S = 2.2690(2)	5.9	3.4	
	1[d]	Ni – C = 1.7901(8)	3.7	-1.4	8.2
	1	Ni – O = 2.781(1)	7.4	2.0	
	4	Ni – S = 2.2700(2)	8.2	5.7	
	1[d]	Ni – C = 1.7977(8)	3.7	-1.4	7.3
	1	Ni – O = 2.768(1)	8.6	3.2	
	5	Ni – S = 2.2710(3)	10.2	7.7	
	1	Ni – C = 1.7845(8)	4.3	-0.8	8.6
	3	Ni – S = 2.2611(3)	6.3	3.8	
	1	Ni – Fe = 2.5586(7)	7.9	6.4	
	1	Ni – C = 1.7946(8)	4.1	-1.0	7.3
	4	Ni – S = 2.2640(3)	8.8	6.3	
	1	Ni – Fe = 2.554(1)	9.6	8.1	

Table S8

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	1[d]	Ni – C = 1.785(6)	20.0	14.9	12.1
	5	Ni – S = 2.2703(4)	10.8	8.3	
	1	Ni – Fe = 2.533(2)	11.5	10.0	
4	1[c]	Ni – C = 1.7769(9)	4.8	-0.3	8.2
	1	Ni – O = 2.952(2)	13.5	8.1	
	3	Ni – S = 2.2580(3)	6.5	4.0	
	1	Ni – Fe = 2.5534(6)	6.3	4.8	
	1[c]	Ni – C = 1.7945(8)	4.1	-1.0	7.3
	1	Ni – O = 2.970(2)	344.1	338.7	
	4	Ni – S = 2.2640(3)	8.8	6.3	
	1	Ni – Fe = 2.554(1)	9.6	8.1	
	1[c]	Ni – C = 1.7967(8)	3.5	-1.6	7.4
	1	Ni – O = 2.972(2)	189.6	184.2	
	5	Ni – S = 2.2683(4)	11.1	8.6	
	1	Ni – Fe = 2.532(1)	11.0	9.5	
	1[d]	Ni – C = 1.7821(8)	4.2	-0.9	5.6
	1	Ni – O = 2.898(1)	4.4	-1.0	
	3	Ni – S = 2.2546(3)	6.9	4.4	
	1	Ni – Fe = 2.5398(7)	5.4	3.9	

Table S8

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	1[d]	Ni – C = 1.7868(8)	3.5	-1.6	6.1
	1	Ni – O = 2.870(2)	7.1	1.7	
	4	Ni – S = 2.2657(5)	9.7	7.2	
	1	Ni – Fe = 2.514(1)	8.8	7.3	
	1[d]	Ni – C =	No Fit		
	1	Ni – O =			
	5	Ni – S =			
	1	Ni – Fe =			
	1[d]	Ni – C = 1.817(1)	6.6	1.5	3.6
	1	Ni – S = 2.1788(4)	-1.0	-3.5	
	2	Ni – S = 2.3085(3)	0.6	-1.9	
	1	Ni – Fe = 2.5878(8)	8.1	6.6	
	1[d]	Ni – C = 1.812(1)	6.4	1.3	3.2
	2	Ni – S = 2.2183(3)	1.5	-1.0	
	1	Ni – S = 2.3441(4)	-1.6	-4.1	
	1	Ni – Fe = 2.5938(8)	7.7	6.2	
	1[d]	Ni – C = 1.807(1)	4.1	-1.0	6.0
	1	Ni – S = 2.1715(8)	2.2	-0.3	
	3	Ni – S = 2.2995(5)	4.8	2.3	
	1	Ni – Fe = 2.567(2)	10.9	9.4	

Table S8

Shell	N	r (Å)	σ^2(x 10^3 Å^2)	$\Delta\sigma^2$(x 10^3 Å^2)	GOF
	1[d]	Ni – C = 1.805(1)	4.1	-1.0	6.0
	2	Ni – S = 2.2038(5)	3.9	1.4	
	2	Ni – S = 2.3272(7)	3.0	0.5	
	1	Ni – Fe = 2.572(2)	<u>10.9</u>	9.4	
	1[d]	Ni – C = 1.804(1)	4.1	-1.0	5.9
	3	Ni – S = 2.2315(4)	5.8	3.3	
	1	Ni – S = 2.3507(9)	1.5	-1.0	
	1	Ni – Fe = 2.577(2)	<u>10.8</u>	9.3	

[a]Fits were generated using k^3 Fourier-filtered data (FT = 2 – 14.3 Å^{-1}, BT = 1.1 – 2.6 Å, uncorrected for phase shifts). σ^2 is the root mean square disorder in the Ni-X distance; $\Delta\sigma^2$ is σ^2 relative to calculated values for reference compounds; GOF = $1/\sigma^2 \sum_{i=1}^{N}\left[y_{\exp}(i) - y_{theo}(i)\right]^2$ (see text). The accuracy of distances determined by EXAFS for atoms in the first coordination sphere of the metal are limited to ± 0.02 Å by the theoretical phase parameters. The refinements generally show precisions that are less than 0.02 Å for well-ordered shells, thus differences in distances between samples using equivalent fits are more accurate than the absolute distances. [b] Underlined values are approaching physical insignificance. Large values of σ^2 suggest that the shell involved has a coordination number that is too large or is badly disordered. For CO ligands the values of σ^2 for atoms in the same coordination sphere were constrained to a single value. [c]Refinement was performed by holding the C-O distance at a constant value (1.175 Å) and varying the Ni-C bond length. [d]Refinement was performed by varying the Ni-C and Ni-O distances of the CO ligand independently.

Table S8

Table S9. FEFF pathways used in fitting model data from tris(2-diphenylphosphinoethyl)amino nickel(0) carbonyl*

File	amp ratio	nlegs	r effective	Paths
Feff 1	**100.00**	**2**	**1.7398**	**Ni -> C -> Ni**
Feff 2	86.439	2	2.2048	Ni -> P -> Ni
Feff 3	**85.433**	**2**	**2.2153**	**Ni -> P -> Ni**
Feff 4	84.664	2	2.2235	Ni -> P -> Ni
Feff 5	**37.612**	**2**	**2.9118**	**Ni -> O -> Ni**
Feff 6	**100.00**	**3**	**2.9149**	**Ni -> O -> C -> Ni**
Feff 7	**67.470**	**4**	**2.9179**	**Ni -> C -> O -> C -> Ni**
Feff 8	4.639	4	3.4797	Ni->C->Ni->C->Ni

*Pathways calculated by FEFF 6. Bold face paths were used in fitting model data.

Table S10. FEFF pathways used in fitting *C. vinosum* Hydrogenase data*

File	amp ratio	nlegs	r effective	Paths
Feff 1	100.000	2	1.7398	Ni -> C -> Ni
Feff 5	37.612	2	2.9118	Ni -> O -> Ni
Feff 6	100.00	3	2.9149	Ni -> O -> C -> Ni
Feff 7	67.470	4	2.9179	Ni -> C -> O -> C -> Ni
Feff 9	98.615	2	2.2815	Ni -> S -> Ni
Feff 10	39.470	2	2.9758	Ni -> Fe -> Ni
Feff 11	100.00	2	2.0193	Ni -> O -> Ni

*FEFF 6 calculated pathways for CO, including multiple scattering paths, were obtained from tris(2-diphenylphosphinoethyl)amino nickel(0) carbonyl (Table S9). Single scattering paths for S, Fe, and O were obtained from FEFF 6 calculations using the structurally characterized models listed in the experimental section.